# The Chemistry of Powder and Explosives

BY

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VOLUME I

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## PREFACE

The present book is primarily for chemists. It has been written in response to the need for a textbook for the course in powder and explosives which the author has given for about twenty years (nearly every year since the first World War) to fourth-year and graduate students of chemistry and of chemical engineering at the Massachusetts Institute of Technology. The students have had comprehensive courses in inorganic, organic, and physical chemistry. The book has been written for the purpose of informing chemists, already well trained, concerning the modes of behavior of explosive substances and concerning the phenomena, both chemical and physical, which they exhibit. No effort has been made to describe the use of explosives in ammunition and in blasting beyond the minimum of description which is needed to make clear the modes of their behavior, and no account has been included of the chemical-engineering aspects of their manufacture.

The original plan of the book called for nine chapters, as follows:

I. Properties of Explosives
II. Black Powder
III. Pyrotechnics
IV. Nitric Esters
V. Smokeless Powder
VI. Dynamite and Other High Explosives
VII. Ammonium Nitrate and Nitroamines
VIII. Primary Explosives, Detonators, and Primers
IX. Aromatic Nitro Compounds

The chapter on aromatic nitro compounds, which it was thought would be the longest in the book, was written first; after that, the next in length, the chapter on pyrotechnics; and finally, the remainder was undertaken from the beginning in the order that was planned. The present very active defense program, and the fact that many young chemists not previously experienced with explosives will soon be working with them, have made it

appear desirable to publish the material already assembled as Volume I of a book entitled "The Chemistry of Powder and Explosives." The five chapters listed above as IV, V, VI, VII, and VIII will be published as soon as possible as Volume II.

The present book is elementary in the sense that it contains nothing which is not the common knowledge of those who are skilled either in chemistry or in the manufacture and use of explosives. Yet it is believed to supply an adequate basis (as far as the subjects of its four chapters are concerned) upon which a chemist commencing work in an explosives laboratory or in the explosives industry may build up, out of the very circumstances of his employment, a further and more specialized knowledge. It is hoped that the book (within its limitations of subject) will help to fit the young chemist for a job in which he can grow. The growth will be in knowledge too technical for inclusion here.

The chapter on pyrotechnics has been made as full as possible. It contains much which will not be found elsewhere, but it limits its discussion to civil pyrotechnics—for several reasons. Civil pyrotechnics is a much broader subject than military pyrotechnics. Military pyrotechnics differ in no important respect from similar devices for civil and recreational purposes. Their varieties are few. Artifices which are not now used for military purposes may some day be applied to the uses of war, and a broad knowledge of civil pyrotechnics plus an acquaintance with the military necessities will determine the applications.

Workers with explosives will perhaps think that I have included in the chapter on pyrotechnics too much material on the construction of fireworks pieces, but chemists, interested in the manners in which their substances behave, will be tempted to try their hands at making the artifices, and the fireworks makers, aware of the importance of these details, will probably think that the account of them is too meager.

The chapter on aromatic nitro compounds deals with the chemistry of a large and important class of explosive substances, among which TNT stands as the most important of the military high explosives, with tetryl second in importance, while the whole class includes substances which are used, or may be used, in shells, bombs, grenades, and other devices of war. The precise manner in which they are loaded, the amounts which are used,

the details of the construction of the devices, etc., are known to those who are concerned with such matters. But the practices change. The principles of the use of the materials, and the physical and chemical properties of the substances upon which the principles depend, do not change—and they are the proper subject matter of the present book.

The aim of the present book has been to describe as clearly and interestingly as possible, and as fully as seemed profitable, the modes of behavior, both physical and chemical, of explosive substances, whether these modes find practical application or not. Historical material has been included where it was thought that it contributed to this end, and has not been included elsewhere or for any other reason.

I am indebted to many friends to whom I wish to make grateful acknowledgment of information, of pictures, and of criticism. Dr. C. G. Storm of Washington, D. C., has read the entire manuscript and has made many helpful suggestions. Dr. Walter O. Snelling of Allentown, Pennsylvania, has read the chapter on aromatic nitro compounds, has kindly prepared the specimen to illustrate the Munroe effect, and has made the photographs from which the two figures are reproduced. Allen F. Clark of Bridgewater, Massachusetts, has read the chapter on pyrotechnics and has supplied many formulas and much other information. His brother, George J. J. Clark, of Whitman, Massachusetts, has furnished several pictures of operations at the plant of the National Fireworks Company, while the *Boston Globe* with his consent has supplied others, and a third brother, Wallace Clark of Chicago, Illinois, has given information relative to the manufacture of Chinese firecrackers and the pictures which illustrate the process. George W. Weingart of New Orleans, Louisiana, has supplied information in his letters, and has given permission to use material from his "Dictionary and Manual of Fireworks," and A. St. H. Brock of London, England, has given permission to quote from his "Pyrotechnics: The History and Art of Firework Making." I am indebted to the Atlas Powder Company, the Ensign-Bickford Company, to E. I. du Pont de Nemours and Company, to the Trojan Powder Company, to the Western Cartridge Company, and to the U. S. Bureau of Mines for pictures, and to the *Journal of the American Chemical Society*, to *Industrial and Engineering Chemistry*, to the *Journal of Chemical Education*,

to the *Journal of the Franklin Institute*, to *Army Ordnance*, to the U. S. Bureau of Mines, and to the University of Pennsylvania Press for permission to quote or to cite from their publications. My thanks are also due to Professor Warren K. Lewis for reading the entire proof.

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CAMBRIDGE, MASSACHUSETTS
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# CHAPTER I

## PROPERTIES OF EXPLOSIVES

### Definition

An explosive is a material, either a pure single substance or a mixture of substances, which is capable of producing an explosion by its own energy.

It seems unnecessary to define an explosion, for everyone knows what it is—a loud noise and the sudden going away of things from the place where they have been. Sometimes it may only be the air in the neighborhood of the material or the gas from the explosion which goes away. Our simple definition makes mention of the one single attribute which all explosives possess. It will be necessary to add other ideas to it if we wish to describe the explosive properties of any particular substance. For example, it is not proper to define an explosive as a substance, or a mixture of substances, which is capable of undergoing a sudden transformation with the production of heat *and* gas. The production of heat alone by the inherent energy of the substance which produces it will be enough to constitute the substance an explosive. Cuprous acetylide explodes by decomposing into copper and carbon and heat, no gas whatever, but the sudden heat causes a sudden expansion of the air in the neighborhood, and the result is an unequivocal explosion. All explosive substances produce heat; nearly all of them produce gas. The change is invariably accompanied by the liberation of energy. The products of the explosion represent a lower energy level than did the explosive before it had produced the explosion. Explosives commonly require some stimulus, like a blow or a spark, to provoke them to liberate their energy, that is, to undergo the change which produces the explosion, but the stimulus which "sets off" the explosive does not contribute to the energy of the explosion. The various stimuli to which explosives respond and the manners of their responses in producing explosions provide a convenient basis for the classification of these interesting materials.

Since we understand an explosive material to be one which is capable of producing an explosion by its own energy, we have opened the way to a consideration of diverse possibilities. An explosive perfectly capable of producing an explosion may liberate its energy without producing one. Black powder, for example, may burn in the open air. An explosion may occur without an explosive, that is, without any material which contains intrinsically the energy needful to produce the explosion. A steam boiler may explode because of the heat energy which has been put into the water which it contains. But the energy is not intrinsic to water, and water is not an explosive. Also, we have explosives which do not themselves explode. The explosions consist in the sudden ruptures of the containers which confine them, as happens in a Chinese firecracker. Fire, traveling along the fuse (note the spelling) reaches the black powder—mixture of potassium nitrate, sulfur, and charcoal—which is wrapped tightly within many layers of paper; the powder burns rapidly and produces gas. It burns very rapidly, for the heat resulting from the burning of the first portion cannot get away, but raises the temperature of the next portion of powder, and a rise of temperature of 10°C. more than doubles the velocity of a chemical reaction. The temperature mounts rapidly; gas is produced suddenly; an explosion ensues. The powder burns; the cracker explodes. And in still other cases we have materials which themselves explode. The molecules undergo such a sudden transformation with the liberation of heat, or of heat and gas, that the effect is an explosion.

## Classification of Explosives

I. **Propellants** or *low explosives* are combustible materials, containing within themselves all oxygen needful for their combustion, which burn but do not explode, and function by producing gas which produces an explosion. Examples: black powder, smokeless powder. Explosives of this class differ widely among themselves in the rate at which they deliver their energy. There are slow powders and fast powders for different uses. The kick of a shotgun is quite different from the persistent push against the shoulder of a high-powered military rifle in which a slower-burning and more powerful powder is used.

II. **Primary explosives** or *initiators* explode or detonate when

they are heated or subjected to shock. They do not burn; sometimes they do not even contain the elements necessary for combustion. The materials themselves explode, and the explosion results whether they are confined or not. They differ considerably in their sensitivity to heat, in the amount of heat which they give off, and in their *brisance*, that is, in the shock which they produce when they explode. Not all of them are brisant enough to initiate the explosion of a high explosive. Examples: mercury fulminate, lead azide, the lead salts of picric acid and trinitroresorcinol, *m*-nitrophenyldiazonium perchlorate, tetracene, nitrogen sulfide, copper acetylide, fulminating gold, nitrosoguanidine, mixtures of potassium chlorate with red phosphorus or with various other substances, the tartarates and oxalates of mercury and silver.

III. **High explosives** *detonate* under the influence of the shock of the explosion of a suitable primary explosive. They do not function by burning; in fact, not all of them are combustible, but most of them can be ignited by a flame and in small amount generally burn tranquilly and can be extinguished easily. If heated to a high temperature by external heat or by their own combustion, they sometimes explode. They differ from primary explosives in not being exploded readily by heat or by shock, and generally in being more brisant and powerful. They exert a mechanical effect upon whatever is near them when they explode, whether they are confined or not. Examples: dynamite, trinitrotoluene, tetryl, picric acid, nitrocellulose, nitroglycerin, liquid oxygen mixed with wood pulp, fuming nitric acid mixed with nitrobenzene, compressed acetylene and cyanogen, ammonium nitrate and perchlorate, nitroguanidine.

It is evident that we cannot describe a substance by saying that it is "very explosive." We must specify whether it is sensitive to fire and to shock, whether it is really powerful or merely brisant, or both, whether it is fast or slow. Likewise, in the discussions in the present book, we must distinguish carefully between sensitivity, stability, and reactivity. A substance may be extremely reactive chemically but perfectly stable in the absence of anything with which it may react. A substance may be exploded readily by a slight shock, but it may be stable if left to itself. Another may require the shock of a powerful detonator

to make it explode but may be subject to spontaneous decomposition.

The three classes of explosive materials overlap somewhat, for the behavior of a number of them is determined by the nature of the stimuli to which they are subjected and by the manner in which they are used. Black powder has probably never been known, even in the hideous explosions which have sometimes occurred at black powder mills, to do anything but burn. Smokeless powder which is made from colloided nitrocellulose, especially if it exists in a state of fine subdivision, is a vigorous high explosive and may be detonated by means of a sufficiently powerful initiator. In the gun it is lighted by a flame and functions as a propellant. Nitroglycerin, trinitrotoluene, nitroguanidine, and other high explosives are used in admixture with nitrocellulose in smokeless powders. Fulminate of mercury if compressed very strongly becomes "dead pressed" and loses its power to detonate from flame, but retains its power to burn, and will detonate from the shock of the explosion of less highly compressed mercury fulminate. Lead azide, however, always explodes from shock, from fire, and from friction.

Some of the properties characteristic of explosives may be demonstrated safely by experiment.

A sample of commercial black powder of moderately fine granulation, say FFF, may be poured out in a narrow train, 6 inches or a foot long, on a sheet of asbestos paper or a wooden board. When one end of the train is ignited, the whole of it appears to burn at one time, for the flame travels along it faster than the eye can follow. Commercial black powder is an extremely intimate mixture; the rate of its burning is evidence of the effect of intimacy of contact upon the rate of a chemical reaction. The same materials, mixed together as intimately as it is possible to mix them in the laboratory, will burn much more slowly.

Six parts by weight of potassium nitrate, one of sulfur (roll brimstone), and one of soft wood (willow) charcoal are powdered separately and passed through a silk bolting-cloth. They are then mixed, ground together in a mortar, and again passed through the cloth; and this process is repeated. The resulting mixture, made into a train, burns fairly rapidly but by no means in a single flash. The experiment is most convincing if a train of commercial black powder leads into a train of this laboratory powder, and the black powder is ignited by means of a piece of *black match* leading from the end of the train and extending beyond the edge of the surface on which the powder is placed. The

black match may be ignited easily by a flame, whereas black powder on a flat surface is often surprisingly difficult to light.

Black match may be made conveniently by twisting three or four strands of fine soft cotton twine together, impregnating the resulting cord with a paste made by moistening *meal powder*[1] with water, wiping off the excess of the paste, and drying while the cord is stretched over a frame. A slower-burning black match may be made from the laboratory powder described above, and is satisfactory for experiments with explosives. The effect of temperature on the rate of a chemical reaction may be demonstrated strikingly by introducing a 12-inch length of black match into a 10-inch glass or paper tube (which need not fit it tightly); when the match is ignited, it burns in the open air at a moderate rate, but, as soon as the fire reaches the point where the tube prevents the escape of heat, the flame darts through the tube almost instantaneously, and the gases generally shoot the burning match out of the tube.

Cuprous acetylide, of which only a very small quantity may be prepared safely at one time, is procured by bubbling acetylene into an ammoniacal solution of cuprous chloride. It precipitates as a brick-red powder. The powder is collected on a small paper filter and washed with water. About 0.1 gram of the material, still moist, is transferred to a small iron crucible—the rest of the cuprous acetylide ought to be destroyed by dissolving in dilute nitric acid—and the crucible is placed on a triangle over a small flame. As soon as the material has dried out, it explodes, with a loud report, causing a dent in the bottom of the crucible.

A 4-inch filter paper is folded as if for filtration, about a gram of FFF black powder is introduced, a 3-inch piece of black match is inserted, and the paper is twisted in such manner as to hold the powder together in one place in contact with the end of the match. The black match is lighted and the package is dropped, conveniently, into an empty pail. The powder burns with a hissing sound, but there is no explosion for the powder was not really confined. The same experiment with about 1 gram of potassium picrate gives a loud explosion. All metallic picrates are primary explosives, those of the alkali metals being the least violent. Potassium picrate may be prepared by dissolving potassium carbonate in a convenient amount of water, warming almost to boiling, adding picric acid in small portions at a time as long as it dissolves with effervescence, cooling the solution, and collecting the crystals and drying them by exposure to the air. For safety's sake,

[1] Corning mill dust, the most finely divided and intimately incorporated black powder which it is possible to procure. Lacking this, black sporting powder may be ground up in small portions at a time in a porcelain mortar.

quantities of more than a few grams ought to be kept under water, in which the substance is only slightly soluble at ordinary temperatures.

About a gram of trinitrotoluene or of picric acid is heated in a porcelain crucible. The substance first melts and gives off combustible vapors which burn when a flame is applied but go out when the flame is removed. A small quantity of trinitrotoluene, say 0.1 gram, may actually be sublimed if heated cautiously in a test tube. If heated quickly and strongly, it decomposes or explodes mildly with a "zishing" sound and with the liberation of soot.

One gram of powdered picric acid and as much by volume of litharge (PbO) are mixed carefully on a piece of paper by turning the powders over upon themselves (not by stirring). The mixture is then poured in a small heap in the center of a clean iron sand-bath dish. This is set upon a tripod, a lighted burner is placed beneath it, and the operator retires to a distance. As soon as the picric acid melts and lead picrate forms, the material explodes with an astonishing report. The dish is badly dented or possibly punctured.

## A Complete Round of Ammunition

The manner in which explosives of all three classes are brought into use will be made clearer by a consideration of the things

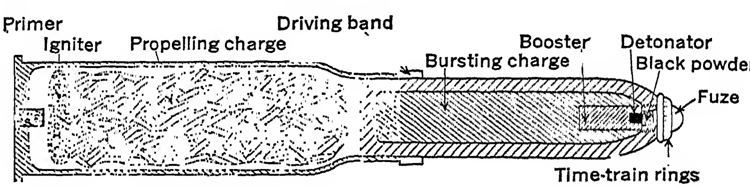



FIGURE 1. Diagram of an Assembled Round of High-Explosive Ammunition. The picture is diagrammatic, for the purpose of illustrating the functions of the various parts, and does not correspond exactly to any particular piece of ammunition.

which happen when a round of H.E. (high-explosive) ammunition is fired. The brass cartridge case, the steel shell with its copper driving band and the fuze screwed into its nose are represented diagrammatically in the accompanying sketch. Note the spelling of fuze: a *fuze* is a device for initiating the explosion of high-explosive shells or of bombs, shrapnel, mines, grenades, etc.; a *fuse* is a device for communicating fire. In cases where the shell is expected to penetrate armor plate or other obstruction, and not to explode until after it has penetrated its target, the nose

of the shell is pointed and of solid steel, and the fuze is screwed into the base of the shell—a base-detonating fuze. The fuze which we wish here to discuss is a point combination fuze, *point* because it is at the nose of the shell, and *combination* because it is designed to explode the shell either after a definite interval of flight or immediately on impact with the target.

The impact of the *firing pin* or trigger upon the *primer cap* in the base of the cartridge case produces fire, a quick small spurt of flame which sets fire to the black powder which is also within the primer. This sets fire to the powder or, in the case of bagged charges, to the *igniter*—and this produces a large hot flame which sweeps out into the chamber of the gun or cartridge, sweeps around the large grains of smokeless powder, and sets fire to them all over their surface. In a typical case the primer cap contains a mixture of mercury fulminate with antimony sulfide and potassium chlorate. The fulminate explodes when the mixture is crushed; it produces fire, and the other ingredients of the composition maintain the fire for a short interval. The igniter bag in our diagram is a silk bag containing black powder which takes fire readily and burns rapidly. The igniter and the bag containing the smokeless powder are made from silk because silk either burns or goes out—and leaves no smoldering residue in the barrel of the gun after the shot has been fired. For different guns and among different nations the igniters are designed in a variety of ways, many of which are described in the books which deal with guns, gunnery, and ammunition. Sometimes the igniter powder is contained in an integral part of the cartridge case. For small arms no igniter is needed; the primer ignites the propellant. For large guns no cartridge case is used; the projectile and the propelling charge are loaded from the breech, the igniter bag being sewed or tied to the base end of the bag which contains the powder, and the *primer* being fitted in a hole in the breechblock by which the gun is closed.

The smokeless powder in our diagram is a dense, progressive-burning, colloided straight nitrocellulose powder, in cylindrical grains with one or with seven longitudinal perforations. The flame from the igniter lights the grains, both on the outer surfaces which commence to burn inward and in the perforations which commence to enlarge, burning outward. The burning at first is slow. As the pressure increases, the projectile starts to move.

The rifling in the barrel of the gun bites into the soft copper driving band, imparting a rotation to the projectile, and the rate of rotation increases as the projectile approaches the muzzle. As heat accumulates in the chamber of the gun, the powder burns faster and faster; gas and heat and pressure are produced for some time at an accelerated rate, and the projectile acquires acceleration continuously. It has its greatest velocity at the moment when it leaves the muzzle. The greatest pressure, however, occurs at a point far back from the muzzle where the gun is of correspondingly stronger construction than at its open end. The duration of the burning of the powder depends upon its *web thickness,* that is, upon the thickness between the single central perforation and the sides of the cylindrical grain, or, in the multiperforated powders, upon the thickness between the perforations. The powder, if properly designed, is burned completely at the moment when the projectile emerges from the muzzle.

The combination fuze contains two primer caps, and devices, more or less free to move within the fuze, by which these may be fired. When the shell starts to move, everything within it undergoes *setback,* and tends to lag because of its inertia. The fuze contains a piece of metal with a point or firing pin on its rearmost end, held in place by an almost complete ring set into its sides and in the sides of the cylindrical space through which it might otherwise move freely. This, with its primer cap, constitutes the *concussion* element. The setback causes it to pull through the ring; the pin strikes the cap; fire is produced and communicates with a train of slow-burning black powder of special composition (fuze powder) the length of which has been previously adjusted by turning the *time-train rings* in the head of the fuze. The powder train, in a typical case, may burn for any particular interval up to 21 seconds, at the end of which time the fire reaches a chamber or magazine which is filled with ordinary black powder. This burns rapidly and produces a large flame which strikes through to the detonator, containing mercury fulminate or lead azide, which explodes and causes the shell to detonate while it is in flight. The head of the fuze may also be adjusted in such manner that the fire produced by the concussion element will finally burn to a dead end, and the shell in that case

will explode only in consequence of the action of the *percussion* element when it hits the target.

When the shell strikes any object and loses velocity, everything within it still tends to move forward. The percussion element consists of a metal cylinder, free to move backward and forward through a short distance, and of a primer cap, opposite the forward end of the cylinder and set into the metal in such fashion that the end of the cylinder cannot quite touch it. If this end of the cylinder should carry a firing pin, then it would fire the cap, and this might happen if the shell were dropped accidentally—with unfortunate results. When the shell starts to move in the gun, the cylinder lags back in the short space which is allotted to it. The shell rotates during flight. Centrifugal force, acting upon a mechanism within the cylinder, causes a firing pin to rise up out of its forward end. The fuze becomes *armed*. When the shell meets an obstacle, the cylinder rushes forward, the pin strikes the cap, fire is produced and communicates directly to the black powder magazine and to the detonator—and the shell is exploded forthwith.

FIGURE 2. Cross Section of a 155-mm. High-Explosive Shell Loaded with TNT.

The high explosive in the shell must be so insensitive that it will tolerate the shock of setback without exploding. Trinitrotoluene (TNT) is generally considered to be satisfactory for all military purposes, except for armor-piercing shells. The explosive must be tightly packed within the shell. There must be no cavities, lest the setback cause the explosive to move violently across the gap and to explode prematurely while the shell is still within the barrel of the gun, or as is more likely, to pull away from the detonator and fail to be exploded by it.

Trinitrotoluene, which melts below the boiling point of water

is generally loaded by pouring the liquid explosive into the shell. Since the liquid contracts when it freezes, and in order to prevent cavities, the shell standing upon its base is supplied at its open end with a paper funnel, like the neck of a bottle, and the liquid TNT is poured until the shell and the paper funnel are both full. After the whole has cooled, the funnel and any TNT which is in it are removed, and the space for the *booster* is bored out with a drill. Cast TNT is not exploded by the explosion of fulminate, which, however, does cause the explosion of granular and compressed TNT. The explosion of granular TNT will initiate the explosion of cast TNT, and the granular material may be used as a booster for that purpose. In practice, tetryl is generally preferred as a booster for military use. It is more easily detonated than TNT, more brisant, and a better initiator. Boosters are used even with high explosives which are detonated by fulminate, for they make it possible to get along with smaller quantities of this dangerous material.

## Propagation of Explosion

When black powder burns, the first portion to receive the fire undergoes a chemical reaction which results in the production of hot gas. The gas, tending to expand in all directions from the place where it is produced, warms the next portion of black powder to the *kindling* temperature. This then takes fire and burns with the production of more hot gas which raises the temperature of the next adjacent material. If the black powder is confined, the pressure rises, and the heat, since it cannot escape, is communicated more rapidly through the mass. Further, the gas- and heat-producing chemical reaction, like any other chemical reaction, doubles its rate for every 10° (approximate) rise of temperature. In a confined space the combustion becomes extremely rapid, but it is still believed to be combustion in the sense that it is a phenomenon dependent upon the transmission of heat.

The explosion of a primary explosive or of a high explosive, on the other hand, is believed to be a phenomenon which is dependent upon the transmission of pressure or, perhaps more properly, upon the transmission of shock.[2] Fire, friction, or shock,

[2] The effects of static pressure and of the rate of production of the pressure have not yet been studied much, nor is there information concerning the pressures which occur within the mass of the explosive while it is exploding.

acting upon, say, fulminate, in the first instance cause it to undergo a rapid chemical transformation which produces hot gas, and the transformation is so rapid that the advancing front of the mass of hot gas amounts to a wave of pressure capable of initiating by its shock the explosion of the next portion of fulminate. This explodes to furnish additional shock which explodes the next adjacent portion of fulminate, and so on, the explosion advancing through the mass with incredible quickness. In a standard No. 6 blasting cap the explosion proceeds with a velocity of about 3500 meters per second.

If a sufficient quantity of fulminate is exploded in contact with trinitrotoluene, the shock induces the trinitrotoluene to explode, producing a shock adequate to initiate the explosion of a further portion. The explosive wave traverses the trinitrotoluene with a velocity which is actually greater than the velocity of the initiating wave in the fulminate. Because this sort of thing happens, the application of the principle of the booster is possible. If the quantity of fulminate is not sufficient, the trinitrotoluene either does not detonate at all or detonates incompletely and only part way into its mass. For every high explosive there is a minimum quantity of each primary explosive which is needed to secure its certain and complete denotation. The best initiator for one high explosive is not necessarily the best initiator for another. A high explosive is generally not its own best initiator unless it happens to be used under conditions in which it is exploding with its maximum *velocity of detonation.*

## Detonating Fuse

Detonating fuse consists of a narrow tube filled with high explosive. When an explosion is initiated at one end by means of a detonator, the explosive wave travels along the fuse with a high velocity and causes the detonation of other high explosives which lie in its path. Detonating fuse is used for procuring the almost simultaneous explosion of a number of charges.

Detonating fuse is called *cordeau détonant* in the French language, and *cordeau* has become the common American designation for it. Cordeau has been made from lead tubes filled with trinitrotoluene, from aluminum or block tin tubes filled with picric acid, and from tubes of woven fabric filled with nitrocellulose or with pentaerythrite tetranitrate (PETN). In this country the Ensign-Bickford Company, at Simsbury, Connecticut, manufac-

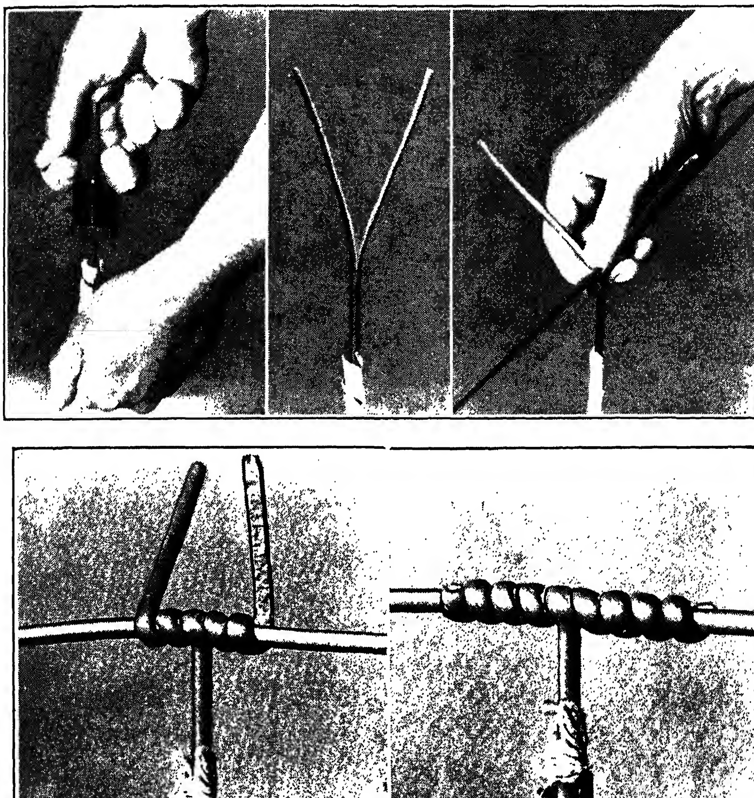
tures *Cordeau-Bickford,* a lead tube filled with TNT, and *Primacord-Bickford,*[3] a tube of waterproof textile filled with finely powdered PETN. The cordeau is made by filling a large lead pipe (about 1 inch in diameter) with molten TNT, allowing to cool, and drawing down in the manner that wire is drawn. The finished tube is tightly packed with finely divided crystalline TNT. Cordeau-Bickford detonates with a velocity of about 5200 meters per second (17,056 feet or 3.23 miles), Primacord-Bickford with a velocity of about 6200 meters per second (20,350 feet or 3.85 miles). These are not the maximum velocities of detonation of the explosives in question. The velocities would be greater if the tubes were wider.

Detonating fuse is fired by means of a blasting cap held snugly and firmly against its end by a *union* of thin copper tubing crimped into place. Similarly, two ends are spliced by holding them in contact within a *coupling.* The ends ought to touch each other, or at least to be separated by not more than a very small space, for the explosive wave of the detonating fuse cannot be depended upon to throw its initiating power across a gap of much more than ⅛ inch.

When several charges are to be fired, a single main line of detonating fuse is laid and branch lines to the several charges are connected to it. The method by which a branch is connected to a main line of cordeau is shown in Figures 3, 4, 5, 6, and 7. The main line is not cut or bent. The end of the branch is slit in two (with a special instrument designed for this purpose) and is opened to form a V in the point of which the main line is laid—and there it is held in place by the two halves of the slit branch cordeau, still filled with TNT, wound around it in opposite directions. The connection is made in this manner in order that the explosive wave, traveling along the main line, may strike the

[3] These are not to be confused with *Bickford fuse* or *safety fuse* manufactured by the same company, which consists of a central thread surrounded by a core of black powder enclosed within a tube of woven threads, surrounded by various layers of textile, waterproof material, sheathing, etc. This is *miner's fuse,* and is everywhere known as Bickford fuse after the Englishman who invented the machine by which such fuse was first woven. The most common variety burns with a velocity of about 1 foot per minute. When the fire reaches its end, a spurt of flame about an inch long shoots out for igniting black powder or for firing a blasting cap.

branch line squarely against the length of the column of TNT, and so provoke its detonation. If the explosive wave were traveling from the branch against the main line (as laid), it would



FIGURES 3, 4, 5, 6, and 7. Method of Connecting a Branch to a Main Line of Cordeau. (Courtesy Ensign-Bickford Company.) FIGURE 3. Slitting the Branch Line. FIGURE 4. The Slit End Open. FIGURE 5. The Main Line in Place. FIGURE 6. Winding the Splice. FIGURE 7. The Finished Junction.

strike across the column of TNT and would shatter it, but would be less likely to make it explode. For connecting a branch line of Primacord, it is satisfactory to make a half hitch of the end around the main line.

A circle of detonating fuse around a tree will rapidly strip off a belt of heavy bark, a device which is sometimes useful in the

control of insect pests. If the detonating fuse is looped successively around a few blocks of TNT or cartridges of dynamite, and if these are strung around a large tree, the tree may be felled very quickly in an emergency. In military operations it may be desirable to "deny a terrain to the enemy" without occupying it oneself, and the result may be accomplished by scattering mustard gas over the area. For this purpose, perhaps during the night, a long piece of Primacord may be laid through the area, looped here and there in circles upon which tin cans of mustard gas (actually a liquid) are placed. The whole may be fired, when desired, by a single detonator, and the gas adequately dispersed.

## Velocity of Detonation

If the quantity of the primary explosive used to initiate the explosion of a high explosive is increased beyond the minimum necessary for that result, the velocity with which the resulting explosion propagates itself through the high explosive is correspondingly increased, until a certain optimum is reached, depending upon the physical state of the explosive, whether cast or powdered, whether compressed much or little, upon the width of the column and the strength of the material which confines it, and of course upon the particular explosive which is used. By proper adjustment of these conditions, by pressing the powdered explosive to the optimum density (which must be determined by experiment) in steel tubes of sufficiently large diameter, and by initiating the explosion with a large enough charge of dynamite or other booster (itself exploded by a blasting cap), it is possible to secure the maximum velocity of detonation. This ultimate maximum is of less interest to workers with explosives than the maximum found while experimenting with paper cartridges, and it is the latter maximum which is generally reported. The physical state and density of the explosive, and the temperature at which the determinations were made, must also be noted if the figures for the velocity of detonation are to be reproducible.

Velocities of detonation were first measured by Berthelot and Vieille,[4] who worked first with gaseous explosives and later with liquids and solids. They used a Boulengé chronograph the precision of which was such that they were obliged to employ long

[4] Berthelot, "Sur la force des matières explosives," 2 vols., third edition, Paris, 1883, Vol. 1, p. 133. Cf. *Mém. poudres,* 4, 7 (1891).

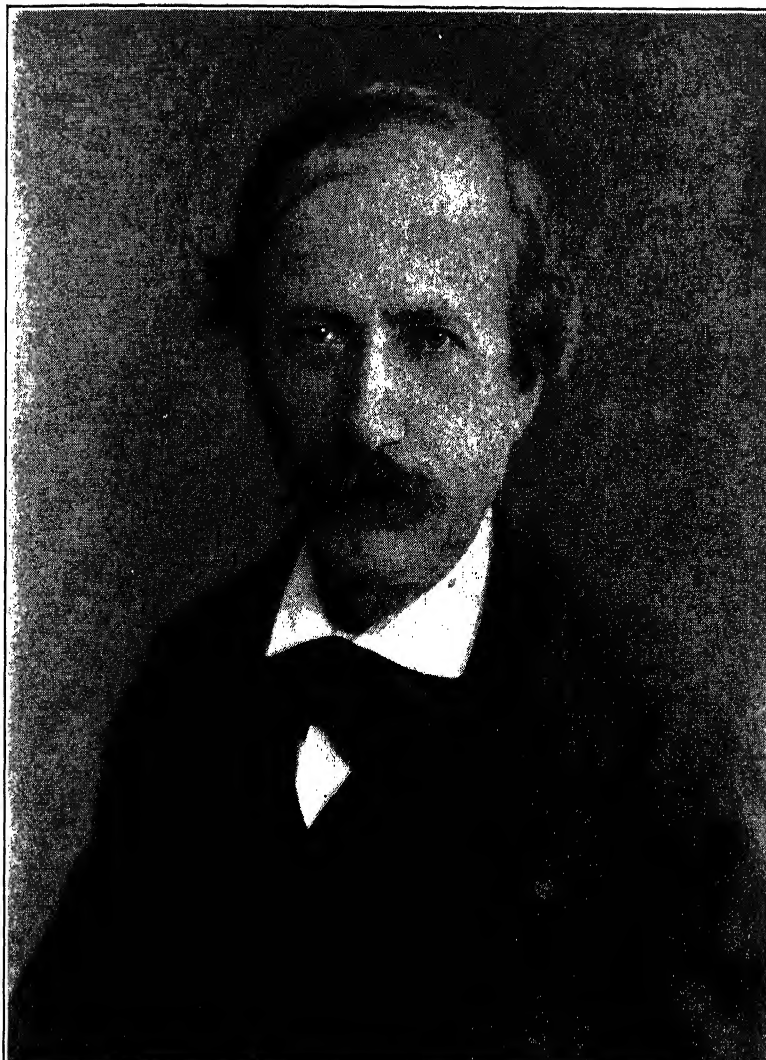


Figure 8. Pierre-Eugéne Marcellin Berthelot (1827-1907) (Photo by P. Nadar, Paris). Founder of thermochemistry and the science of explosives. He synthesized acetylene and benzene from their elements, and alcohol from ethylene, studied the polyatomic alcohols and acids, the fixation of nitrogen, the chemistry of agriculture, and the history of Greek, Syriac, Arabic, and medieval chemistry. He was a Senator of France, Minister of Public Instruction, Minister of Foreign Affairs, and Secretary of the Academy of Sciences, and is buried in the Panthéon at Paris.

columns of the explosives. The Mettegang recorder now commonly used for these measurements is an instrument of greater precision and makes it possible to work with much shorter cartridges of the explosive materials. This apparatus consists essentially of a strong, well-turned and balanced, heavy cylinder of steel which is rotated by an electric motor at a high but exactly known velocity. The velocity of its smoked surface relative to a platinum point which almost touches it may be as much as 100 meters per second. The explosive to be tested is loaded in a cylindrical cartridge. At a known distance apart two thin copper wires are passed through the explosive at right angles to the axis of the cartridge. If the explosive has been cast, the wires are bound tightly to its surface. Each of the wires is part of a closed circuit through an inductance, so arranged that, when the circuit is broken, a spark passes between the platinum point and the steel drum of the chronograph. The spark makes a mark upon the smoked surface. When the explosive is now fired by means of a detonator at the end of the cartridge, first one and then the other of the two wires is broken by the explosion, and two marks are made on the rotating drum. The distance between these marks is measured with a micrometer microscope. The duration of time which corresponds to the movement of the surface of the rotating drum through this distance is calculated, and this is the time which was required for the detonation of the column of known length of explosive which lay between the two wires. From this, the velocity of detonation in meters per second is computed easily.

Since a chronograph is expensive and time-consuming to use, the much simpler method of Dautriche,[5] which depends upon a comparison of the unknown with a standard previously measured by the chronograph, finds wide application. Commercial cordeau is remarkably uniform. An accurately measured length, say 2 meters, of cordeau of known velocity of detonation is taken, its midpoint is marked, and its ends are inserted into the cartridge of the explosive which is being tested, at a known distance apart, like the copper wires in the absolute method (Figure 9). The middle portion of the loop of cordeau is made straight and is laid upon a sheet of lead (6-8 mm. thick), the marked midpoint being

[5] *Mém. poudres,* **14**, 216 (1907); *Comp. rend.,* **143**, 641 (1906).

placed upon a line scratched in the lead plate at right angles to the direction of the cordeau. When the detonator in the end of the cartridge of explosive is fired, the explosive wave first encounters one end of the cordeau and initiates its explosion from this end, then proceeds through the cartridge, encounters the other end of the cordeau, and initiates its explosion from that end. The explosive waves from the two ends of the cordeau meet one another and mark the point of their meeting by an extra-deep, sharp furrow in the lead plate, perhaps by a hole punched

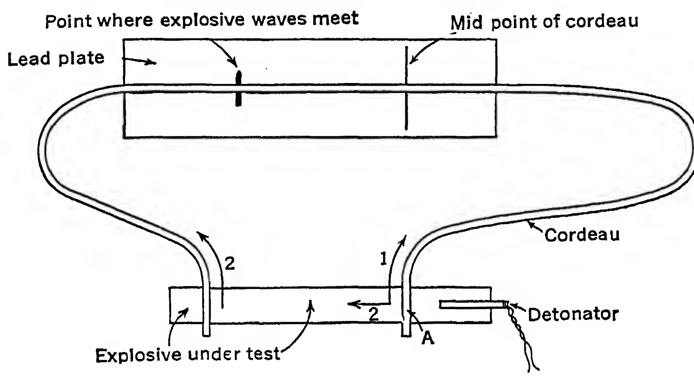



FIGURE 9. Dautriche Method of Measuring Velocity of Detonation. From the point $A$ the explosion proceeds in two directions: (1) along the cordeau (of known velocity of detonation), and (2) through the cartridge of explosive which is being tested and then along the cordeau. When the two waves in the cordeau meet, they make a mark in the lead plate upon which the cordeau is resting.

through it. The distance of this point is measured from the line where the midpoint of the cordeau was placed. Call this distance $d$. It is evident that, from the moment when the near end of the cordeau started to detonate, one explosive wave traveled in the cordeau for a distance equal to one-half the length of the cordeau plus the distance $d$, while the other explosive wave, during the same interval of time, traveled in the explosive under examination a distance equal to the distance between the inserted ends of cordeau, then in the cordeau a distance equal to one-half its length minus the distance $d$. The times required for the passage of the explosive waves in the cordeau are calculated from the known velocity of detonation of the cordeau used; thence the time required for the detonation of the column of explosive which

stood between the ends of the cordeau; thence the velocity of detonation in meters per second.

Velocities of detonation have recently been measured by high-speed photography of the explosions through a slit, and by other devices in which the elapsed times are measured by means of a cathode-ray oscillograph.

## The Munroe Effect

The mark which explosive waves, traveling toward each other on the same piece of cordeau, make at the point where they meet is evidently due to the fact that they spread out sideways at the point of their encounter. Their combined forces produce an effect greater than either alone could give. The behavior of jets of water, shot against each other under high pressure, supplies a very good qualitative picture of the impact of explosive waves. If the waves meet at an angle, the resultant wave, stronger than either, goes off in a direction which could be predicted from a consideration of the parallelogram of forces. This is the explanation of the Munroe effect.

Charles Edward Munroe,[6] while working at the Naval Torpedo Station at Newport, discovered in 1888 that if a block of guncotton with letters countersunk into its surface is detonated with its lettered surface against a steel plate, the letters are indented into the surface of the steel. Similarly, if the letters are raised above the surface of the guncotton, by the detonation they are reproduced in relief on the steel plate, embossed and raised above the neighboring surface. In short, the greatest effects are produced on the steel plate at the points where the explosive material stands away from it, at the points precisely where explosive waves from different directions meet and reinforce each other. Munroe found that by increasing the depth of the concavity in the explosive he was able to produce greater and greater effects on the plate, until finally, with a charge which was pierced completely through, he was able to puncture a hole through it.[7] By introducing lace, ferns, coins, etc., between the flat surface of a

[6] For biographical notice by C. A. Browne, see *J. Am. Chem. Soc.*, **61**, 731 (1939).

[7] Cf. article by Marshall, "The Detonation of Hollow Charges," *J. Soc. Chem. Ind.*, **29**, 35 (1920).

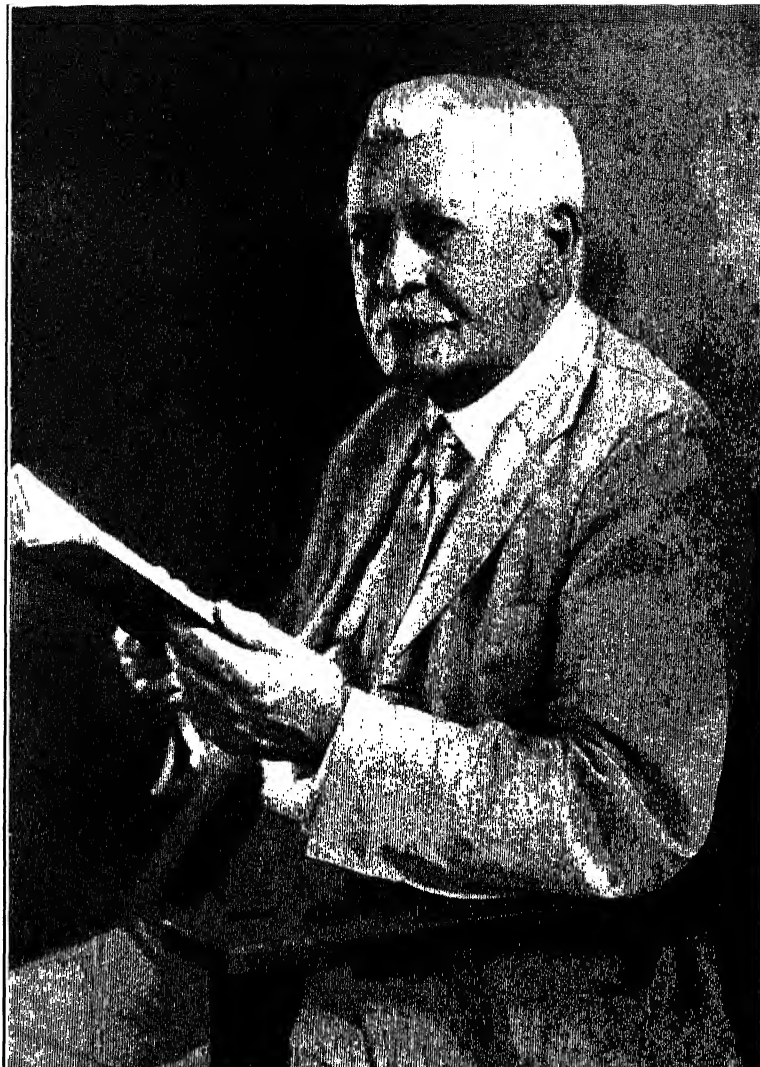


FIGURE 10. Charles Edward Munroe (1849-1938). Leader in the development of explosives in the United States. Invented *indurite*, a variety of smokeless powder, and discovered the Munroe effect. Professor of chemistry at the U. S. Naval Academy, Annapolis, Maryland, 1874-1886; chemist at the Naval Torpedo Station and Naval War College, Newport, Rhode Island, 1886-1892; professor of chemistry at George Washington University, 1892-1917; and chief explosives chemist of the U. S. Bureau of Mines in Washington, 1919-1933. Author and co-author of many very valuable publications of the Bureau of Mines.

block of explosive and pieces of armor plate, Munroe was able to secure embossed reproductions of these delicate materials. Several fine examples of the Munroe effect, prepared by Munroe himself, are preserved in a fire screen at the Cosmos Club in Washington.

The effect of hollowed charges appears to have been rediscovered, probably independently, by Egon Neumann, who claimed it as an original discovery, and its application in explosive technique was patented by the Westfälisch-Anhaltische Sprengstoff-

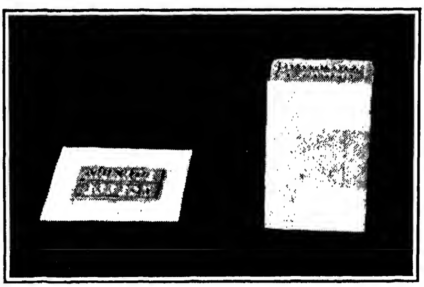


FIG. 11

FIG. 12

FIGURES 11 and 12. Munroe Effect. (Courtesy Trojan Powder Company). FIGURE 11. Explosive Enclosed in Pasteboard Wrapper. Note that the letters incised into the surface of the explosive are in mirror writing, like words set in type, in order that the printing may be normal. A steel plate after a charge like that pictured was exploded against it, the incised surface being next to the plate. FIGURE 12. A section of steel shafting after a charge like that represented in FIGURE 11 had been exploded upon it, the incised surface of the explosive being next to the steel.

A. G. in 1910.[8] Neumann, working with blocks of TNT having conical indentations but not complete perforations, found that such blocks blew holes through wrought-iron plates, whereas solid blocks of greater actual weight only bent or dented them.

It has been recommended that torpedoes be loaded with charges hollowed in their forward ends. Advantage is taken of the Munroe effect in the routine blasting of oil wells, and, intentionally or not, by every explosives engineer who initiates an explosion by means of two or more electric blasting caps, fired simultaneously, at different positions within the same charge.

[8] Ger. Pat. Anm. W. 36,269 (1910); Brit. Pat. 28,030 (1911). Neumann, *Z. angew. Chem.*, 2238 (1911); *Z. ges. Schiess- u. Sprengstoffw.*, 183 (1914).

## Sensitivity Tests

Among the important tests which are made on explosives are the determinations of their sensitivity to impact and to temperature, that is, of the distance through which a falling weight must drop upon them to cause them to explode or to inflame, and of the temperatures at which they inflame, explode, or "puff" spontaneously. At different places different machines and apparatus are used, and the numerical results differ in consequence from laboratory to laboratory.

For the falling weight or *impact* or *drop test* a 2-kilogram weight is generally used. In a typical apparatus the explosive undergoing the test is contained in a hole in a steel block, a steel plunger or piston is pressed down firmly upon it, and it is directly upon this plunger that the weight is dropped. A fresh sample is taken each time, and material which has not exploded from a single impact is discarded. A drop of 2 to 4 cm. will explode mercury fulminate, one of about 70 to 80 cm. will cause the inflammation of black powder, and one of 60 to 180 cm. will cause the explosion of TNT according to the physical state of the sample.

For determining the *temperature of ignition*, a weighed amount of the material is introduced into a copper capsule (a blasting cap shell) and this is thrust into a bath of Wood's metal previously heated to a known temperature. If no explosion occurs within 5 seconds (or other definite interval), the sample is removed, the temperature of the bath is raised 5° (usually), and a fresh sample in a fresh copper capsule is tried. Under these conditions (that is, within a 5-second interval), 4F black powder takes fire at $190° \pm 5°$, and 30-caliber straight nitrocellulose smokeless powder at $315° \pm 5°$. In another method of carrying out the test, the capsule containing the explosive is introduced into the metal bath at 100°, the temperature is raised at a steady and regulated rate, and the temperature at which the explosive decomposition occurs is noted. When the temperature is raised more rapidly, the inflammation occurs at a higher temperature, as indicated by the following table.[9] The fact that explosives are more sensitive to shock and to friction when they are warm is doubtless due to the same ultimate causes.

[9] van Duin, Dissertation, Utrecht, 1918, p. 89. The experiments were carried out with 0.1-gram samples in glass tubes.

| | Temperature of Ignition Heated from 100° at 20° per minute | at 5° per minute |
|---|---|---|
| Trinitrotoluene | 321° | 304° |
| Picric acid | 316° | 309° |
| Tetryl | 196° | 187° |
| Hexanitrodiphenylamine | 258° | 250° |
| Hexanitrodiphenyl sulfide | 319° | 302° |
| Hexanitrodiphenyl sulfone | 308° | 297° |

Substances like trinitrotoluene, picric acid, and tetryl, which are intrinsically stable at ordinary temperatures, decompose slowly if they are heated for considerable periods of time at temperatures below those at which they inflame. This, of course, is a matter of interest, but it is a property of all samples of the substance, does not vary greatly between them, and is not made the object of routine testing. Nitrocellulose and many nitric esters, however, appear to be intrinsically unstable, subject to a spontaneous decomposition which is generally slow but may be accelerated greatly by the presence of impurities in the sample. For this reason, nitrocellulose and smokeless powder are regularly subjected to *stability tests* for the purpose, not of establishing facts concerning the explosive in question, but rather for determining the quality of the particular sample.[10]

[10] The routine tests which are carried out on military explosives are described in U. S. War Department Technical Manual TM9-2900, "Military Explosives." The testing of explosives for sensitivity, explosive power, etc., is described in the *Bulletins* and *Technical Papers* of the U. S. Bureau of Mines. The student of explosives is advised to secure from the Superintendent of Documents, Washington, D. C., a list of the publications of the Bureau of Mines, and then to supply himself with as many as may be of interest, for they are sold at very moderate prices. The following are especially recommended. Several of these are now no longer procurable from the Superintendent of Documents, but they may be found in many libraries.

*Bull.* 15. "Investigations of Explosives Used in Coal Mines," by Clarence Hall, W. O. Snelling, and S. P. Howell.

*Bull.* 17. "A Primer on Explosives for Coal Miners," by Charles E. Munroe and Clarence Hall.

*Bull.* 48. "The Selection of Explosives Used in Engineering and Mining Operations," by Clarence Hall and Spencer P. Howell.

*Bull.* 59. "Investigations of Detonators and Electric Detonators," by Clarence Hall and Spencer P. Howell.

*Bull.* 66. "Tests of Permissible Explosives," by Clarence Hall and Spencer P. Howell.

## Tests of Explosive Power and Brisance

For estimating the total energy of an explosive, a test in the manometric bomb probably supplies the most satisfactory single indication. It should be remembered that total energy and actual effectiveness are different matters. The effectiveness of an explosive depends in large part upon the rate at which its energy is liberated.

The high pressures developed by explosions were first measured by means of the Rodman gauge, in which the pressure caused a hardened-steel knife edge to penetrate into a disc of soft copper. The depth of penetration was taken as a measure of the pressure to which the apparatus had been subjected. This gauge was improved by Nobel, who used a copper cylinder placed between a fixed and a movable steel piston. Such *crusher gauges* are at present used widely, both for measuring the maximum pressures produced by explosions within the confined space of the manometric bomb and for determining the pressures which exist in the barrels of guns during the proof firing of powder. The small copper cylinders are purchased in large and uniform lots, their deformations under static pressures are determined and plotted in a chart, and the assumption is made that the sudden pressures resulting from explosions produce the same deformations as static pressures of the same magnitudes. Piezoelectric gauges, in which the pressure on a tourmaline crystal or on discs of quartz produces an electromotive force, have been used in work with manometric bombs and for measuring the pressures which exist in the chambers of guns. Other gauges, which depend

*Bull.* 80. "A Primer on Explosives for Metal Miners and Quarrymen," by Charles E. Munroe and Clarence Hall.

*Bull.* 346. "Physical Testing of Explosives at the Bureau of Mines Explosives Experiment Station, Bruceton, Pa.," by Charles E. Munroe and J. E. Tiffany.

*Tech. Paper* 125. "The Sand Test for Determining the Strength of Detonators," by C. G. Storm and W. C. Cope.

*Tech. Paper* 234. "Sensitiveness of Explosives to Frictional Impact," by S. P. Howell.

On this subject the book "Testing Explosives" by C. E. Bichel, English translation by A. Larnsen, London, 1905, will be found of value, as will also the book of Berthelot, already cited, and many important papers in *Mémorial des poudres* and *Zeitschrift für das gesamte Schiess- und Sprengstoffwesen.*

upon the change of electrical resistance of a conducting wire, are beginning to find application.

The manometric bomb is strongly constructed of steel and has a capacity which is known accurately. In order that the pressure resulting from the explosion may have real significance, the *density of loading*, that is, the number of grams of explosive per cubic centimeter of volume, must also be reported. The pressures produced by the same explosive in the same bomb are in general not directly proportional to the density of loading. The temperatures in the different cases are certainly different, and the compositions of the hot gaseous mixtures depend upon the pressures which exist upon them and determine the conditions of the equilibria between their components. The water in the gases can be determined, their volume and pressure can be measured at ordinary temperature, and the temperature of the explosion can be calculated roughly if the assumptions are made that the gas laws hold and that the composition of the cold gases is the same as that of the hot. If the gases are analyzed, and our best knowledge relative to the equilibria which exist between the components is assumed to be valid for the whole temperature range, then the temperature produced by the explosion can be calculated with better approximation.

Other means of estimating and comparing the capacity of explosives for doing useful work are supplied by the tests with the *ballistic pendulum*[11] and by the Trauzl and small lead block tests. The first of these is useful for comparing a new commercial explosive with one which is standard; the others give indications which are of interest in describing both commercial explosives and pure explosive substances.

In the *Trauzl lead block test* (often called simply the lead block test) 10 grams of the explosive, wrapped in tinfoil and stemmed with sand, is exploded by means of an electric detonator in a cylindrical hole in the middle of a cylindrical block of lead, and the enlargement of the cavity, measured by pouring in water from a graduate and corrected for the enlargement which is ascribable to the detonator alone, is reported. For the standard test, the blocks are cast from chemically pure lead, 200 mm. in height and 200 mm. in diameter, with a central hole made by the mold, 125 mm. deep and 25 mm. in diameter. The test is

[11] *U. S. Bur. Mines Bull.* 15, pp. 79-82.

applicable only to explosives which detonate. Black powder and other explosives which burn produce but little effect, for the gases blow out the stemming and escape. The test is largely one of brisance, but for explosives of substantially equal brisance it gives some indication of their relative power. An explosive of great brisance but little power will create an almost spherical pocket at the bottom of the hole in the block, while one of less brisance and greater power will enlarge the hole throughout its

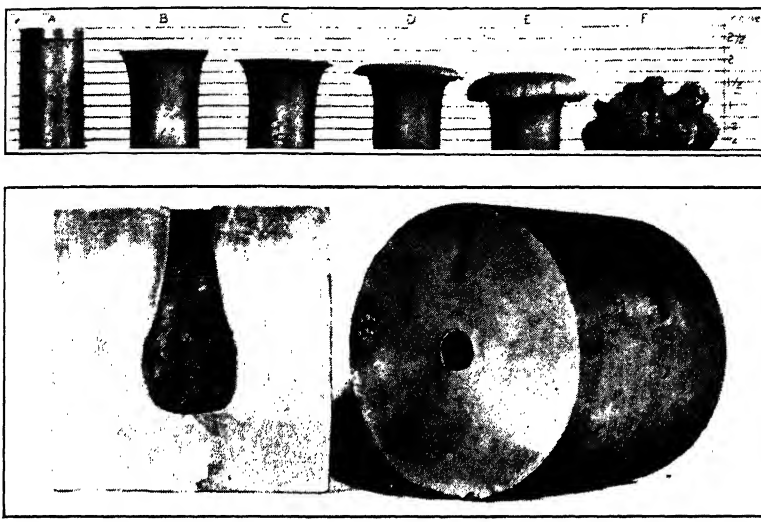


FIGURE 13. Lead Block Tests (above), and Trauzl Tests (below). (Courtesy U. S. Bureau of Mines.)

length and widen its throat at the top of the block. The form of the hole, then, as shown by sectioning the block, is not without significance. The Trauzl test does not give reliable indications with explosives which contain aluminum (such as *ammonal*) or with others which produce very high temperatures, for the hot gases erode the metal, and the results are high.

A small Trauzl block is used for testing commercial detonators.

Another test, known as the *small lead block test*, is entirely a test of brisance. As the test is conducted at the U. S. Bureau of Mines,[12] a lead cylinder 38 mm. in diameter and 64 mm. high is set upright upon a rigid steel support; a disc of annealed steel

[12] *Ibid.*, p. 114.

38 mm. in diameter and 6.4 mm. thick is placed upon it; a strip of manila paper wide enough to extend beyond the top of the composite cylinder and to form a container at its upper end is wrapped and secured around it; 100 grams of explosive is placed

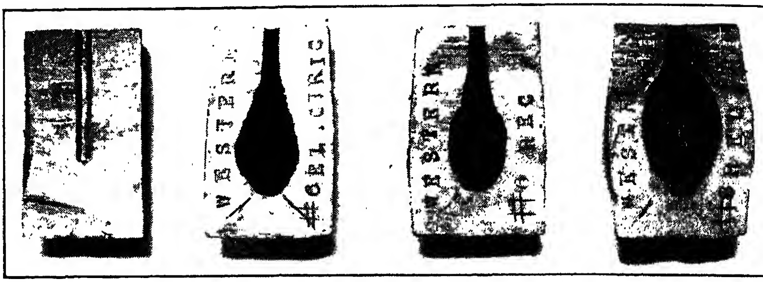


FIGURE 14. Small Trauzl Tests of Detonators. (Courtesy Western Cartridge Company.)

in this container and fired, without tamping, by means of an electric detonator. The result is reported as the compression of the lead block, that is, as the difference between its height before and its height after the explosion. The steel disc receives the force of the explosion and transmits it to the lead cylinder. Without it, the lead cylinder would be so much deformed that its height could not be measured.

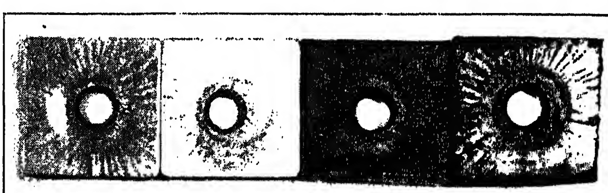


FIGURE 15. Aluminum Plate and Lead Plate Tests of Detonators. (Courtesy Atlas Powder Company.)

In the *lead plate test of detonators*, the detonator is fired while standing upright on a plate of pure lead. Plates 2 to 6 mm. thick are used, most commonly 3 mm. A good detonator makes a clean-cut hole through the lead. The metal of the detonator case is blown into small fragments which make fine and characteristic markings on the lead plate radiating away from the place where

the detonator stood. With a good detonator, the surface of the lead plate ought to show no places where it has been torn roughly

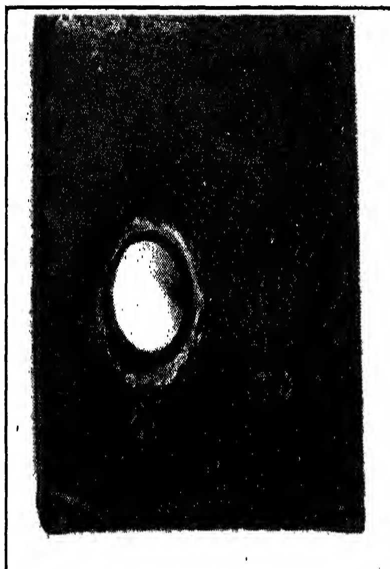


FIGURE 16. Effect of Detonator on Lead Plate 10 cm. Distant from Its End. The diameter of the hole is about 1½ times the diameter of the detonator which was fired. The lead has splashed up around the hole in much the same fashion as placid water splashes when a pebble is dropped into it. Note the numerous small splashes on the lead plate where it was struck by fragments of the detonator casing.

by large fragments of the case. Similar tests are often carried out with plates of aluminum.

# CHAPTER II

## BLACK POWDER

The discovery that a mixture of potassium nitrate, charcoal, and sulfur is capable of doing useful mechanical work is one of the most important chemical discoveries or inventions of all time. It is to be classed with the discovery or invention of pottery, which occurred before the remote beginning of history, and with that of the fixation of nitrogen by reason of which the ecology of the human race will be different in the future from what it has been throughout the time that is past. Three great discoveries signalized the break-up of the Middle Ages: the discovery of America, which made available new foods and drugs, new natural resources, and new land in which people might multiply, prosper, and develop new cultures; the discovery of printing, which made possible the rapid and cheap diffusion of knowledge; and the discovery of the controllable force of gunpowder, which made huge engineering achievements possible, gave access to coal and to minerals within the earth, and brought on directly the age of iron and steel and with it the era of machines and of rapid transportation and communication. It is difficult to judge which of these three inventions has made the greatest difference to mankind.

Black powder and similar mixtures were used in incendiary compositions, and in pyrotechnic devices for amusement and for war, long before there was any thought of applying their energy usefully for the production of mechanical work. The invention of guns—and it seems to be this invention which is meant when "the discovery of gunpowder" is mentioned—did not follow immediately upon the discovery of the composition of black powder. It is possible that other applications antedated it, that black powder was used in petards for blowing down gateways, drawbridges, etc., or in simple operations of blasting, before it was used for its ballistic effect.

## Berthold Schwarz

The tradition that the composition of black powder was discovered and that guns were invented about 1250 (or 1350 or even later) by Berthold Schwarz, a monk of Freiburg i. Br., in Germany, is perpetuated by a monument at that place. Constantin Anklitzen assumed the name of Berthold when he joined the Franciscan order, and was known by his confreres as *der schwarzer Berthold* because of his interest in black magic. The records of the Franciscan chapter in Freiburg were destroyed or scattered before the Reformation, and there are no contemporaneous accounts of the alleged discovery. Concerning the absence of documents, Oesper[1] says:

> If he is a purely legendary inventor the answer is obvious. However, history may have taken no interest in his doings because guns were said to be execrable inventions and their employment (except against the unbelievers) was decried as destructive of manly valor and unworthy of an honorable warrior. Berthold was reputed to have compounded powder with Satan's blessing, and the clergy preached that as a coworker of the Evil One he was a renegade to his profession and his name should be forgotten. There is a tradition that he was imprisoned by his fellow monks, and some say he made his diabolic invention while in prison. According to another legend, Berthold blew himself up while demonstrating the power of his discovery; another states that he was executed.
>
> The lovers of fine points may argue over Berthold's existence, but it can be historically established that Freiburg in the fourteenth and fifteenth centuries was a flourishing center for the casting of cannon and the training of gunners.

## Boerhaave on Black Powder

Although black powder has done immeasurable good through its civil uses, it has nevertheless been regarded as an evil discovery because of the easy and unsportsmanlike means which it provides for the destruction of life. Boerhaave, more than two centuries ago, wrote in the modern spirit on the importance of chemistry in war and condemned black powder[2] in a manner

[1] Oesper, *J. Chem. Education,* 16, 305-306 (1939).

[2] Boerhaave, "A New Method of Chemistry," etc., trans. Peter Shaw, London, 1753, Vol. I, pp. 189-191. The quoted passage corresponds to the Latin of Vol. I, pp. 99-101, of the first edition of Boerhaave's "Elementa Chemiae," Leiden, 1732.

similar to that in which some of our latest devices of warfare have been decried in public print.

> It were indeed to be wish'd that our art had been less ingenious, in contriving means destructive to mankind; we mean those instruments of war, which were unknown to the ancients, and have made such havoc among the moderns. But as men have always been bent on seeking each other's destruction by continual wars; and as force, when brought against us, can only be repelled by force; the chief support of war, must, after money, be now sought in chemistry.
>
> *Roger Bacon*, as early as the twelfth century,[3] had found out gunpowder, wherewith he imitated thunder and lightning; but that age was so happy as not to apply so extraordinary a discovery to the destruction of mankind. But two ages afterwards, *Barthol. Schwartz*,[4] a *German* monk and chemist, happening by some accident to discover a prodigious power of expanding in some of this powder which he had made for medicinal uses, he apply'd it first in an iron barrel, and soon after to the military art, and taught it to the *Venetians*. The effect is, that the art of war has since that time turned entirely on this one chemical invention; so that the feeble boy may now kill the stoutest hero: Nor is there anything, how vast and solid soever, can withstand it. By a thorough acquaintance with the power of this powder, that intelligent *Dutch* General *Cohorn* quite alter'd the whole art of fighting; making such changes in the manner of fortification, that places formerly held impregnable, now want defenders. In effect, the power of gun-powder is still more to be fear'd. I tremble to mention the stupendous force of another

[3] Bacon lived in the thirteenth century; we quote the passage as it is printed.

[4] Shaw's footnote (*op. cit.*, p. 190) states:

> What evidently shews the ordinary account of its invention false, is, that *Schwartz* is held to have first taught it to the *Venetians* in the year 1380; and that they first used it in the war against the *Genoese*, in a place antiently called *Fossa Caudeana*, now *Chioggia*. For we find mention of fire arms much earlier: *Peter Messius*, in his *variae lectiones*, relates that *Alphonsus XI.* king of Castile used mortars against the *Moors*, in a siege in 1348; and *Don Pedro*, bishop of *Leon*, in his chronicle, mentions the same to have been used above four hundred years ago, by the people of *Tunis*, in a sea fight against the *Moorish* king of *Sevil*. *Du Cange* adds, that there is mention made of this powder in the registers of the chambers of accounts in *France*, as early as the year 1338.

powder, prepar'd of sulfur, nitre, and burnt lees of wine;[5] to say nothing of the well-known power of *aurum fulminans*. Some person taking a quantity of fragrant oil, chemically procured from spices, and mixing it with a liquor procured from salt-petre, discover'd a thing far more powerful than gun-powder itself; and which spontaneously kindles and

[5] This is *fulminating powder*, made, according to Ure's "Dictionary of Chemistry," first American edition, Philadelphia, 1821:

> by triturating in a warm mortar, three parts by weight of nitre, two of carbonate of potash, and one of flowers of sulfur. Its effects, when fused in a ladle, and then set on fire, are very great. The whole of the melted fluid explodes with an intolerable noise, and the ladle is commonly disfigured, as if it had received a strong blow downwards.

Samuel Guthrie, Jr. (cf. *Archeion*, **13**, 11 ff. [1931]), manufactured and sold in this country large quantities of a similar material. In a letter to Benjamin Silliman dated September 12, 1831 (*Am. J. Sci. Arts*, **21**, 288 ff. [1832]), he says:

> I send you two small phials of nitrated sulphuret of potash, or yellow powder, as it is usually called in this country. . . . I have made some hundred pounds of it, which were eagerly bought up by hunters and sportsmen for *priming* fire arms, a purpose which it answered most admirably; and, but for the happy introduction of powder for priming, which is ignited by percussion, it would long since have gone into extensive use.
>
> With this preparation I have had much to do, and I doubt whether, in the whole circle of experimental philosophy, many cases can be found involving dangers more appalling, or more difficult to be overcome, than melting fulminating powder and saving the product, and reducing the process to a business operation. I have had with it some eight or ten tremendous explosions, and in one of them I received, full in my face and eyes, the flame of a quarter of a pound of the composition, just as it had become thoroughly melted.
>
> The common proportions of 3 parts of nitre, 2 parts of carbonate of potash and 1 part of sulphur, gave a powder three times quicker than common black powder; but, by *melting together* 2 parts of nitre and 1 of carbonate of potash, and when the mass was cold adding to 4½ parts of it, 1 part of sulphur—equal in the 100, to 54.54 dry nitre, 27.27 dry carbonate of potash and 18.19 sulphur—a greatly superior composition was produced, burning no less than eight and one half times quicker than the best common powder. The substances were intimately ground together, and then melted to a *waxy* consistence, upon an iron plate of one inch in thickness, heated over a muffled furnace, taking care to knead the mass assiduously, and remove the plate as often as the bottom of the mass became pretty slippery.
>
> By the previously melting together of the nitre and carbonate of potash, a more intimate union of these substances was effected than could possibly be made by mechanical means, or by the slight melting which was admissible in the after process; and by the slight melting of the whole upon a *thick* iron plate, I was able to conduct the business with facility and safety.
>
> The melted mass, after being cold, is as hard and porous as pumice stone, and is grained with difficulty; but there is a stage when it is cooling in which it is very crumbly, and it should then be powdered upon a board, with a small wooden cylinder, and put up hot, without sorting the grains or even sifting out the flour.

burns with great fierceness, without any application of fire.[6] I shall but just mention a fatal event which lately happen'd in *Germany*, from an experiment made with balsam of sulphur terebinthinated, and confined in a close chemical vessel, and thus exploded by fire; God grant that mortal men may not be so ingenious at their own cost, as to pervert a profitable science any longer to such horrible uses. For this reason I forbear to mention several other matters far more horrible and destructive, than any of those above rehearsed.

## Greek Fire

Fire and the sword have been associated with each other from earliest times. The invention of Greek fire appears to have consisted of the addition of saltpeter to the combustible mixtures already in use, and Greek fire is thus seen as the direct ancestor both of black gunpowder and of pyrotechnic compositions.

The Byzantine historian, Theophanes the Confessor, narrates that "Constantine [Constantine IV, surnamed Pogonatus, the Bearded], being apprised of the designs of the unbelievers against Constantinople, commanded large boats equipped with cauldrons of fire (tubs or vats of fire) and fast-sailing galleys equipped with siphons." The narrative refers to events which occurred in the year 670, or possibly 672. It says for the next year: "At this time Kallinikos, an architect (engineer) from Heliopolis of Syria, came to the Byzantines and having prepared a sea fire (or marine fire) set fire to the boats of the Arabs, and burned these with their men aboard, and in this manner the Byzantines were victorious and found (discovered) the marine fire."[7] The Moslem fleet was destroyed at Cyzicus by the use of this fire which for several centuries afterwards continued to bring victory to the Byzantines in their naval battles with the Moslems and Russians.

Leo's *Tactica*, written about A.D. 900 for the generals of the empire, tells something of the manner in which the Greek fire was to be used in combat.

[6] Shaw's footnote (*op. cit.*, p. 191): "A drachm of compound spirit of nitre being poured on half a drachm of oil of carraway seeds *in vacuo*; the mixture immediately made a flash like gun-powder, and burst the exhausted receiver, which was a glass six inches wide, and eight inches deep."

[7] Quoted by N. D. Cheronis, article entitled "Chemical Warfare in the Middle Ages. Kallinikos's Prepared Fire," *J. Chem. Education*, 14, 360 (1937).

> And of the last two oarsmen in the bow, let the one be the *siphonator*, and the other to cast the anchor into the sea. . . . In any case, let him have in the bow the *siphon* covered with copper, as usual, by means of which he shall shoot the *prepared fire* upon the enemy. And above such siphon (let there be) a false bottom of planks also surrounded by boards, in which the warriors shall stand to meet the oncoming foes. . . . On occasion [let there be] formations immediately to the front [without maneuvers] so, whenever there is need, to fall upon the enemy at the bow and set fire to the ships by means of the *fire of the siphons*. . . . Many very suitable contrivances were invented by the ancients and moderns, with regard to both the enemy's ships and the warriors on them—such as at that time the *prepared fire* which is ejected (thrown) by means of *siphons* with a roar and a lurid (burning) smoke and filling them [the ships] with smoke. . . . They shall use also the other method of small *siphons* thrown (i.e., directed) by hand from behind iron shields and held [by the soldiers], which are called *hand siphons* and have been recently manufactured by our state. For these can also throw (shoot) the *prepared fire* into the faces of the enemy.[8]

Leo also described the use of *strepta*, by which a liquid fire was ejected, but he seemed to have been vague upon the details of construction of the pieces and upon the force which propelled the flame, and, like the majority of the Byzantine writers, he failed to mention the secret ingredient, the saltpeter, upon which the functioning of the fires undoubtedly depended, for their flames could be directed downward as well as upward.

The Byzantines kept their secret well and for a long time, but the Moslems finally learned about it and used the fire against the Christians at the time of the Fifth Crusade. In the Sixth Crusade the army of Saint Louis in Egypt was assailed with incendiaries thrown from ballistae, with fire from tubes, and with grenades of glass and metal, thrown by hand, which scattered fire on bursting. Brock[9] thinks that the fire from tubes operated in the manner of Roman candles. The charge, presumed to be a non-homogeneous mixture of combustible materials with saltpeter, "will, in certain proportions, if charged into a strong tube, give intermittent bursts, projecting blazing masses of the mixture to a

[8] Cheronis, *op. cit.*, p. 362.

[9] A. St. H. Brock, "Pyrotechnics: the History and Art of Firework Making," London, 1922, p. 15.

considerable distance. The writer has seen this effect produced in a steel mortar of $5\frac{1}{2}$ inches diameter, the masses of composition being thrown a distance of upwards of a hundred yards, a considerable range in the days of close warfare." There is no reason to believe that the fire tubes were guns.

### Marcus Graecus

In the celebrated book of Marcus Graecus, *Liber ignium ad comburendos hostes,*[10] Greek fire and other incendiaries are described fully, as is also black powder and its use in rockets and crackers. This work was quoted by the Arabian physician, Mesue, in the ninth century, and was probably written during the eighth.

> Greek fire is made as follows: take sulfur, tartar, sarcocolla, pitch, melted saltpeter, petroleum oil, and oil of gum, boil all these together, impregnate tow with the mixture, and the material is ready to be set on fire. This fire cannot be extinguished by urine, or by vinegar, or by sand. . . .
>
> Flying fire (rockets) may be obtained in the following manner: take one part of colophony, the same of sulfur, and two parts of saltpeter. Dissolve the pulverized mixture in linseed oil, or better in oil of lamium. Finally, the mixture is placed in a reed or in a piece of wood which has been hollowed out. When it is set on fire, it will fly in whatever direction one wishes, there to set everything on fire.

Another mixture corresponds more closely to the composition of black powder. The author even specifies grapevine or willow charcoal which, with the charcoal of black alder, are still the preferred charcoals for making fuze powders and other grades where slow burning is desired.

> Take one pound of pure sulfur, two pounds of grapevine or willow charcoal, and six pounds of saltpeter. Grind these three substances in a marble mortar in such manner as to reduce them to a most subtle powder. After that, the powder in desired quantity is put into an envelope for flying (a rocket) or for making thunder (a cracker). Note that the envelope for flying ought to be thin and long and well-filled with the above-described powder tightly packed, while the envelope for making thunder ought to be short and thick,

[10] Book of fires for burning the enemy, reprinted in full by Hoefer, "Histoire de la chimie," second edition, Paris, 1866, Vol. 1, pp. 517-524, and discussed *ibid.*, Vol. 1, p. 309.

> only half filled with powder, and tightly tied up at both ends with an iron wire. Note that a small hole ought to be made in each envelope for the introduction of the match. The match ought to be thin at both ends, thick in the middle, and filled with the above-described powder. The envelope intended to fly in the air has as many thicknesses (ply) as one pleases; that for making thunder, however, has a great many.

Toward the end of the *Liber ignium* the author gives a slightly different formula for the black powder to be used in rockets.

> The composition of flying fire is threefold. The first composition may be made from saltpeter, sulfur, and linseed oil. These ground up together and packed into a reed, and lighted, will make it ascend in the air. Another flying fire may be made from saltpeter, sulfur, and grapevine or willow charcoal. These materials, mixed and introduced into a papyrus tube, and ignited, will make it fly rapidly. And note that one ought to take three times as much charcoal as sulfur and three times as much saltpeter as charcoal.

### Roger Bacon

Roger Bacon appears to have been the first scholar in northern Europe who was acquainted with the use of saltpeter in incendiary and explosive mixtures. Yet the passage in which he makes specific mention of this important ingredient indicates that toy firecrackers were already in use by the children of his day. In the "Opus Majus," Sixth Part, On Experimental Science, he writes:

> For malta, which is a kind of bitumen and is plentiful in this world, when cast upon an armed man burns him up. The Romans suffered severe loss of life from this in their conquests, as Pliny states in the second book of the Natural History, and as the histories attest. Similarly yellow petroleum, that is, oil springing from the rock, burns up whatever it meets if it is properly prepared. For a consuming fire is produced by this which can be extinguished with difficulty; for water cannot put it out. Certain inventions disturb the hearing to such a degree that, if they are set off suddenly at night with sufficient skill, neither city nor army can endure them. No clap of thunder could compare with such noises. Certain of these strike such terror to the sight that the coruscations of the clouds disturb it incomparably less. . . . We have an example of this in that toy of children which is made in many parts of the world, namely an instrument as

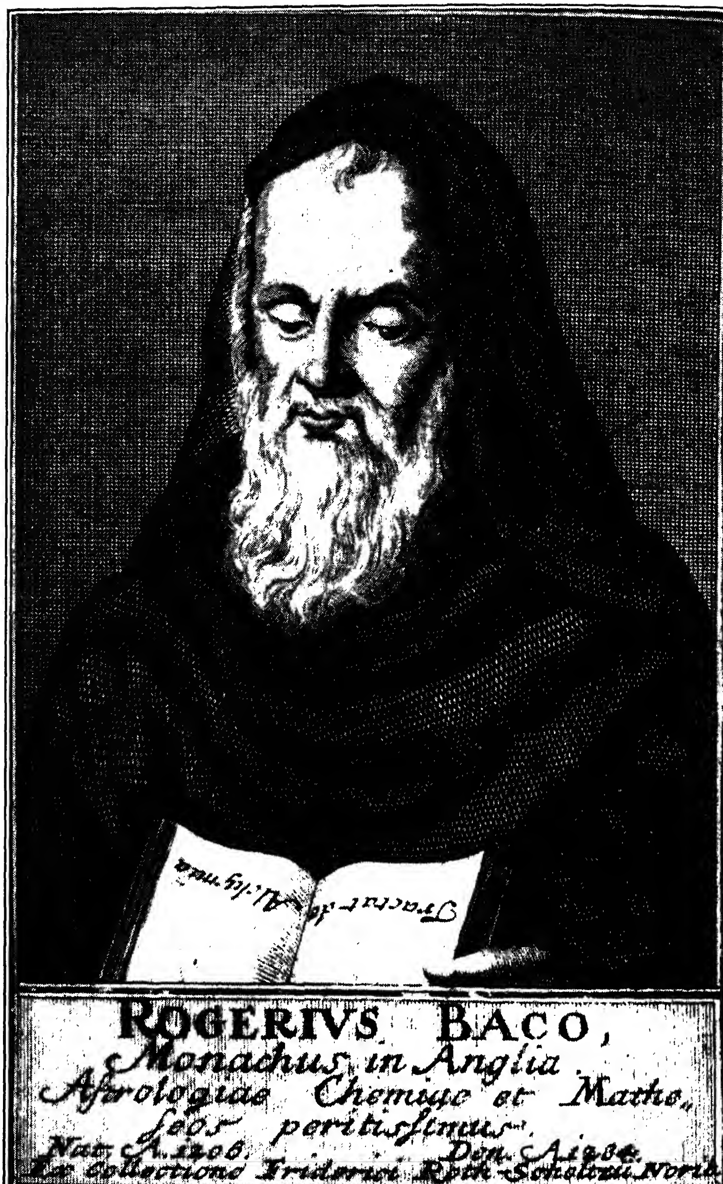



FIGURE 17. Roger Bacon (*c.* 1214-1292). Probably the first man in Latin Europe to publish a description of black powder. He was acquainted with rockets and firecrackers, but not with guns.

> large as the human thumb. From the force of the salt called saltpeter so horrible a sound is produced at the bursting of so small a thing, namely a small piece of parchment, that we perceive it exceeds the roar of sharp thunder, and the flash exceeds the greatest brilliancy of the lightning accompanying the thunder.[11]

A description in cypher of the composition of black powder in the treatise "De nullitate magiae"[12] which is ascribed to Roger Bacon has attracted considerable attention. Whether Bacon wrote the treatise or not, it is certain at any rate that the treatise dates from about his time and certain, too, that much of the material which it contains is to be found in the "Opus Majus." The author describes many of the wonders of nature, mechanical, optical, medicinal, etc., among them incendiary compositions and firecrackers.

> We can prepare from saltpeter and other materials an artificial fire which will burn at whatever distance we please. The same may be made from red petroleum and other things, and from amber, and naphtha, and white petroleum, and from similar materials. . . . Greek fire and many other combustibles are closely akin to these mixtures. . . . For the sound of thunder may be artificially produced in the air with greater resulting horror than if it had been produced by natural causes. A moderate amount of proper material, of the size of the thumb, will make a horrible sound and violent coruscation.

Toward the end of the treatise the author announces his intention of writing obscurely upon a secret of the greatest importance, and then proceeds to a seemingly incoherent discussion of something which he calls "the philosopher's egg." Yet a thoughtful reading between the lines shows that the author is describing the purification of "the stone of Tagus" (saltpeter), and that this material is somehow to be used in conjunction with "certain parts of burned shrubs or of willow" (charcoal) and with the "vapor of pearl" (which is evidently sulfur in the language of the medieval

[11] "The Opus Majus of Roger Bacon," trans. Robert Belle Burke, University of Pennsylvania Press, Philadelphia, 1928, Vol. 2, p. 629.

[12] Cf. "Roger Bacon's Letter Concerning the Marvelous Power of Art and of Nature and Concerning the Nullity of Magic," trans. Tenney L. Davis, Easton, Pennsylvania, 1922.

chemists). The often-discussed passage which contains the black powder anagram is as follows:

> *Sed tamen salis petrae LVRV VO PO VIR CAN VTRIET sulphuris, et sic facies tonitruum et coruscationem: sic facies artificium.*

A few lines above the anagram, the author sets down the composition of black powder in another manner. "Take then of the bones of Adam (charcoal) and of the Calx (sulfur), the same weight of each; and there are six of the Petral Stone (saltpeter) and five of the Stone of Union." The Stone of Union is either sulfur or charcoal, probably sulfur, but it doesn't matter for the context has made it evident that only three components enter into the composition. Of these, six parts of saltpeter are to be taken, five each of the other two. The little problem in algebra supplies a means of checking the solution of the anagram, and it is evident that the passage ought to be read as follows:

> *Sed tamen salis petrae R. VI. PART. V. NOV. CORVLI. ET V. sulphuris, et sic facies tonitruum et coruscationem: sic facies artificium.*
>
> But, however, of saltpeter take six parts, five of young willow (charcoal), and five of sulfur, and so you will make thunder and lightning, and so you will turn the trick.

The 6:5:5 formula is not a very good one for the composition of black powder for use in guns, but it probably gave a mixture which produced astonishing results in rockets and firecrackers, and it is not unlike the formulas of mixtures which are used in certain pyrotechnic pieces at the present time.

Although Roger Bacon was not acquainted with guns or with the use of black powder for accomplishing mechanical work, yet he seems to have recognized the possibilities in the mixture, for the treatise "On the Nullity of Magic" comes to an end with the statement: "Whoever will rewrite this will have a key which opens and no man shuts, and when he will shut, no man opens."[13]

[13] Compare *Revelations*, 3: 7 and 8. "And to the angel of the church in Philadelphia write: These things saith he that is holy, he that is true, he that hath the key of David, he that openeth, and no man shutteth; and shutteth, and no man openeth; I know thy works: behold, I have set before thee an open door, and no man can shut it."

### Development of Black Powder[14]

Guns apparently first came into use shortly after the death of Roger Bacon. A manuscript in the Asiatic Museum at Leningrad, probably compiled about 1320 by Shems ed Din Mohammed, shows tubes for shooting arrows and balls by means of powder. In the library of Christ Church, Oxford, there is a manuscript entitled "De officiis regum," written by Walter de Millemete in 1325, in which a drawing pictures a man applying a light to the touch-hole of a bottle-shaped gun for firing a dart. On February 11, 1326, the Republic of Venice ordered iron bullets and metal cannon for the defense of its castles and villages, and in 1338 cannon and powder were provided for the protection of the ports of Harfleur and l'Heure against Edward III. Cannon were used in 1342 by the Moors in the defense of Algeciras against Alphonso XI of Castile, and in 1346 by the English at the battle of Crécy.

When guns began to be used, experiments were carried out for determining the precise composition of the mixture which would produce the best effect. One notable study, made at Bruxelles about 1560, led to the selection of a mixture containing saltpeter 75 per cent, charcoal 15.62 per cent, and sulfur 9.38 per cent. A few of the formulas for black powder which have been used at various times are calculated to a percentage basis and tabulated below:

| | Saltpeter | Charcoal | Sulfur |
|---|---|---|---|
| 8th century, Marcus Graecus | 66.66 | 22.22 | 11.11 |
| 8th century, Marcus Graecus | 69.22 | 23.07 | 7.69 |
| c. 1252, Roger Bacon | 37.50 | 31.25 | 31.25 |
| 1350, Arderne (laboratory recipe) | 66.6 | 22.2 | 11.1 |
| 1560, Whitehorne | 50.0 | 33.3 | 16.6 |
| 1560, Bruxelles studies | 75.0 | 15.62 | 9.38 |
| 1635, British Government contract | 75.0 | 12.5 | 12.5 |
| 1781, Bishop Watson | 75.0 | 15.0 | 10.0 |

It is a remarkable fact, and one which indicates that the improvements in black powder have been largely in the methods of manufacture, that the last three of these formulas correspond very closely to the composition of all potassium nitrate black powder for military and sporting purposes which is used today. Any considerable deviation from the 6:1:1 or 6:1.2:0.8 formulas

[14] An interesting and well-documented account of the history of black powder and of other explosives may be found in Molinari and Quartieri's "Notizie sugli esplodenti in Italia," Milano, 1913.

produces a powder which burns more slowly or produces less vigorous effects, and different formulas are used for the compounding of powders for blasting and for other special purposes. In this country blasting powder is generally made from sodium nitrate.

John Bate early in the seventeenth century understood the individual functions of the three components of black powder

FIGURE 18. Gunpowder Manufacture, Lorrain, 1630. After the materials had been intimately ground together in the mortar, the mixture was moistened with water, or with a solution of camphor in brandy, or with other material, and formed into grains by rubbing through a sieve.

when he wrote: "The Saltpeter is the Soule, the Sulphur the Life, and the Coales the Body of it."[15] The saltpeter supplies the oxygen for the combustion of the charcoal, but the sulfur is the life, for this inflammable element catches the first fire, communicates it throughout the mass, makes the powder quick, and gives it vivacity.

Hard, compressed grains of black powder are not porous—the sulfur appears to have colloidal properties and to fill completely

[15] John Bate, "The Mysteries of Nature and Art," second edition, London, 1635, p. 95.

the spaces between the small particles of the other components—and the grains are poor conductors of heat. When they are lighted, they burn progressively from the surface. The area of the surface of an ordinary grain decreases as the burning advances, the grain becomes smaller and smaller, the rate of production of gas decreases, and the duration of the whole burning depends upon the dimension of the original grain. Large powder grains which required more time for their burning were used in the larger guns. Napoleon's army used roughly cubical grains 8 mm. thick in its smaller field guns, and cubical or lozenge-shaped grains twice as thick in some of its larger guns. Grains in the form of hexagonal prisms were used later, and the further improvement was introduced of a central hole through the grain in a direction parallel to the sides of the prism. When these single-perforated hexagonal prisms were lighted, the area of the outer surfaces decreased as the burning advanced, but the area of the inner surfaces of the holes actually increased, and a higher rate of production of gas was maintained. Such powder, used in rifled guns, gave higher velocities and greater range than had ever before been possible. Two further important improvements were made: one, the use of multiple perforations in the prismatic grain by means of which the burning surface was made actually to increase as the burning progressed, with a resultant acceleration in the rate of production of the gases; and the other, the use of the slower-burning *cocoa powder* which permitted improvements in gun design. These, however, are purely of historical interest, for smokeless powder has now entirely superseded black powder for use in guns.

If a propellent powder starts to burn slowly, the initial rise of pressure in the gun is less and the construction of the breech end of the gun need not be so strong and so heavy. If the powder later produces gas at an accelerated rate, as it will do if its burning surface is increasing, then the projectile, already moving in the barrel, is able to take up the energy of the powder gases more advantageously and a greater velocity is imparted to it. The desired result is now secured by the use of progressive-burning colloided smokeless powder. Cocoa powder was the most successful form of black powder for use in rifled guns of long range.

Cocoa powder or brown powder was made in single-perforated

hexagonal or octagonal prisms which resembled pieces of milk chocolate. A partially burned brown charcoal made from rye straw was used. This had colloidal properties and flowed under pressure, cementing the grains together, and made it possible to manufacture powders which were slow burning because they contained little sulfur or sometimes even none. The compositions of several typical cocoa powders are tabulated below:

| | Saltpeter | Brown Charcoal | Sulfur |
|---|---|---|---|
| England......... | 79 | 18 | 3 |
| England......... | 77.4 | 17.6 | 5 |
| Germany......... | 78 | 19 | 3 |
| Germany......... | 80 | 20 | 0 |
| France........... | 78 | 19 | 3 |

Cocoa powder was more sensitive to friction than ordinary black powder. Samples were reported to have inflamed from shaking in a canvas bag. Cocoa powder was used in the Spanish-American war, 1898. When its use was discontinued, existing stocks were destroyed, and single grains of the powder are now generally to be seen only in museums.

## Burning of Black Powder

Black powder burns to produce a white smoke. This, of course, consists of extremely small particles of solid matter held temporarily in suspension by the hot gases from the combustion. Since the weight of these solids is equal to more than half of the weight of the original powder, the superiority of smokeless powder, which produces practically no smoke and practically 100 per cent of its weight of hot gas, is immediately apparent. The products of the burning of black powder have been studied by a number of investigators, particularly by Noble and Abel,[16] who showed that the burning does not correspond to any simple chemical reaction between stoichiometrical proportions of the ingredients. Their experiments with RLG powder having the percentage composition indicated below showed that this powder burned to produce (average results) 42.98 per cent of its weight of gases, 55.91 per cent solids, and 1.11 per cent water.

[16] Noble and Abel, *Phil. Trans.*, 1875, 49; 1880, 203; *Mém. poudres*, 1. 193 (1882). See also Debus, *Proc. Roy. Soc.*, 30, 198 (1880).

| | | | |
|---|---|---|---|
| Potassium nitrate | | | 74.430 |
| Potassium sulfate | | | 0.133 |
| Sulfur | | | 10.093 |
| Charcoal | Carbon | 12.398 | 14.286 |
| | Hydrogen | 0.401 | |
| | Oxygen | 1.272 | |
| | Ash | 0.215 | |
| Moisture | | | 1.058 |

Their mean results from the analysis of the gaseous products (percentage by volume) and of the solid products (percentage by weight) are shown in the following tables.

| | |
|---|---|
| Carbon dioxide | 49.29 |
| Carbon monoxide | 12.47 |
| Nitrogen | 32.91 |
| Hydrogen sulfide | 2.65 |
| Methane | 0.43 |
| Hydrogen | 2.19 |

| | |
|---|---|
| Potassium carbonate | 61.03 |
| Potassium sulfate | 15.10 |
| Potassium sulfide | 14.45 |
| Potassium thiocyanate | 0.22 |
| Potassium nitrate | 0.27 |
| Ammonium carbonate | 0.08 |
| Sulfur | 8.74 |
| Carbon | 0.08 |

One gram of the powder in the state in which it was normally used, that is, while containing 1.058 per cent of moisture, produced 718.1 calories and 271.3 cc. of permanent gas measured at 0° and 760 mm. One gram of the completely desiccated powder gave 725.7 calories and 274.2 cc. These results indicate by calculation that the explosion of the powder produces a temperature of about 3880°.

## Uses of Black Powder

Where smoke is no objection, black powder is probably the best substance that we have for communicating fire and for producing a quick hot flame, and it is for these purposes that it is now principally used in the military art. Indeed, the fact that its flame is filled with finely divided solid material makes it more efficient as an igniter for smokeless powder than smokeless powder itself. Standard black powder (made approximately in accordance with the 6:1:1 or the 6:1.2:0.8 formula) is used in *pétards*, as a base charge or expelling charge for shrapnel shells, in saluting and blank fire charges, as the bursting charge of practice shells and bombs, as a propelling charge in certain pyrotechnic pieces, and, either with or without the admixture of other substances which modify the rate of burning, in the time-train

Figure 19. Stamp Mill for Making Black Powder. (Courtesy National Fireworks Company and the *Boston Globe*.) This mill, which makes powder for use in the manufacture of fireworks, consists of a single block of granite in which three deep cup-shaped cavities have been cut. The stamps which operate in these cups are supplied at their lower ends with cylindrical blocks of wood, sections cut from the trunk of a hornbeam tree. These are replaced when worn out. The powder from the mill is called "meal powder" and is used as such in the manufacture of fireworks. Also it is moistened slightly with water and rubbed through sieves to form granular gunpowder for use in making rockets, Roman candles, aerial bombshells, and other artifices.

rings and in other parts of fuzes. Modified black powders, in which the proportion of the ingredients does not approximate to the standard formulas just mentioned, have been used for blasting, especially in Europe, and have been adapted to special uses in pyrotechny. Sodium nitrate powder, *ammonpulver,* and other more remote modifications are discussed later in this chapter or in the chapter on pyrotechnics.

## Manufacture

During the eighteenth century, stamp mills (Figure 19) for incorporating the ingredients of black powder largely superseded the more primitive mortars operated by hand. The meal powder, or *pulverin* as the French call it, was made into gunpowder by moistening slightly and then pressing through sieves.[17] The powder grains were not uniform with one another either in their composition or their density, and could not be expected to give very uniform ballistic results. The use of a heavy wheel mill for grinding and pressing the materials together, and the subsequent pressing of the material into a hard cake which is broken up into grains, represent a great advance in the art and produce hard grains which are physically and ballistically uniform.[18] The operations in the manufacture of black powder as it is carried out at present are briefly as follows:

1. *Mixing* of the powdered materials is accomplished by hand or mechanical blending while they are dampened with enough water to prevent the formation of dust, or the powdered sulfur and charcoal are stirred into a saturated solution of the requisite amount of potassium nitrate at a temperature of about 130°, the hot mass is spread out on the floor to cool, and the lumps are broken up.

2. *Incorporating or Milling.* The usual wheel mill has wheels which weigh 8 or 10 tons each. It takes a charge of 300 pounds of

[17] The French still make *pulverin,* for the preparation of black match and for use in pyrotechnics, by rolling the materials with balls, some of lead and some of lignum vitae, in a barrel of hardwood. They also sometimes use this method for mixing the ingredients before they are incorporated more thoroughly in the wheel mill.

[18] The black powder wheel mill is also used for reducing (under water) deteriorated smokeless powder to a fine meal in order that it may be reworked or used in the compounding of commercial explosives, and for the intimate incorporation of such explosives as the French *schneiderite.*

the mixture. The wheels rotate for about 3 hours at a rate of about 10 turns per minute. Edge runners turn back under the tread of the wheels material which would otherwise work away from the center of the mill. Considerable heat is produced during the milling, and more water is added from time to time to replace that which is lost by evaporation in order that the material may always be moist. The "wheel cake" and "clinker" which result from the milling are broken up into small pieces for the pressing.

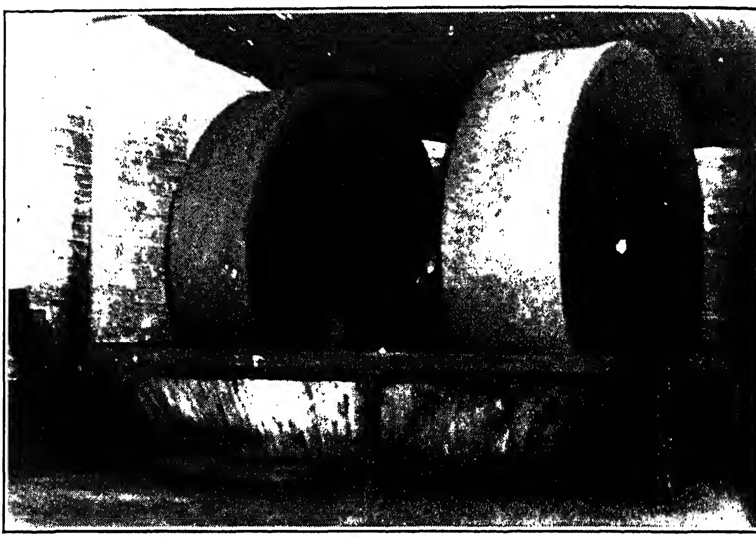


FIGURE 20. Modern Wheel Mill for Making Black Powder. (Courtesy Atlas Powder Company.) The large wheels weigh 10 tons each.

3. *Pressing* is done in a horizontal hydraulic press. Layers of powder are built up by hand between plates of aluminum, and the whole series of plates is pressed in one operation. The apparatus is so designed that fragments of powder are free to fall out at the edges of the plates, and only as much of the material remains between them as will conveniently fill the space. An effective pressure of about 1200 pounds per square inch is applied, and the resulting press cakes are about ¾ inch thick and 2 feet square.

4. *Corning or granulating* is the most dangerous of the operations in the manufacture of black powder. The corning mill is usually situated at a distance from the other buildings, is barri-

caded, and is never approached while the machinery, controlled from a distance, is in operation. The press cake is cracked or granulated between crusher rolls. Screens, shaken mechanically, separate the dust and the coarse pieces from the grains which are of the right size for use. The coarse pieces pass between other crusher rolls and over other screens, four sets of crusher rolls being used. Corning mill dust is used in fuse powder and by the makers of fireworks, who find it superior for certain purposes to other kinds of meal powder.

5. *Finishing.* The granulated powder from the corning mill is rounded or polished and made "bright" by tumbling in a revolving wooden cylinder or barrel. Sometimes it is dried at the same time by forcing a stream of warm air through the barrel. Or the polished powder is dried in wooden trays in a dry-house at 40°. If a glazed powder is desired, the glaze is usually applied before the final drying. To the polished powder, still warm from the tumbling, a small amount of graphite is added, and the tumbling is continued for a short time. Black powder of commerce usually contains about 1 or 1.5 per cent moisture. If it contains less than this, it has a tendency to take up moisture from the air; if it contains much more, its efficiency is affected.

6. *Grading.* The powder is finally rescreened and separated into the different grain sizes, C (coarse), CC, CCC, F (fine), FF or 2F, 3F, 4F, etc. The word *grade* applied to black powder, refers to the grain size, not to the quality.

## Analysis[19]

A powdered sample for analysis may be prepared safely by grinding granulated black powder, in small portions at a time, in a porcelain mortar. The powder may be passed through a 60-mesh sieve and transferred quickly to a weighing bottle without taking up an appreciable amount of moisture.

[19] A test which from ancient times has been applied to black powder is carried out by pouring a small sample onto a cold flat surface and setting fire to it. A good powder ought to burn in a flash and leave no "pearls" or residue of globules of fused salt. A solid residue indicates either that the ingredients have not been well incorporated, or that the powder at some time in its history has been wet (resulting in larger particles of saltpeter than would be present in good powder, the same result as poor incorporation), or that the powder at the time of the test contains an undue amount of moisture.

*Moisture* is determined by drying in a desiccator over sulfuric acid for 3 days, or by drying to constant weight at 60° or 70°, at which temperature 2 hours is usually long enough.

For determining *potassium nitrate*, the weighed sample in a Gooch crucible is washed with hot water until the washings no longer give any test for nitrate,[20] and the crucible with its contents is dried to constant weight at 70°. The loss of weight is equal to potassium nitrate *plus* moisture. In this determination, as in the determination of moisture, care must be taken not to dry the sample too long, for there is danger that some of the sulfur may be lost by volatilization.

*Sulfur* is determined as the further loss of weight on extraction with carbon disulfide in a Wiley extractor or other suitable apparatus. After the extraction, the crucible ought to be allowed to dry in the air away from flames until all the inflammable carbon disulfide has escaped. It is then dried in the oven to constancy of weight, and the residue is taken as *charcoal*. *Ash* is determined by igniting the residue in the crucible until all carbon has burned away. A high result for ash may indicate that the water extraction during the determination of potassium nitrate was not complete. The analytical results may be calculated on a moisture-free basis for a closer approximation to the formula by which the manufacturer prepared the powder.

## Blasting Powder

The 6:1:1 and 6:1.2:08 formulas correspond to the quickest and most vigorous of the black-powder compositions. A slower and cheaper powder is desirable for blasting, and both these desiderata are secured by a reduction in the amount of potassium nitrate. For many years the French government has manufactured and sold three kinds of blasting or mining powder, as follows:

| | Saltpeter | Charcoal | Sulfur |
|---|---|---|---|
| *Forte* | 72 | 15 | 13 |
| *Lente* | 40 | 30 | 30 |
| *Ordinaire* | 62 | 18 | 20 |

In the United States a large part of all black powder for blast-

[20] A few drops, added to a few cubic centimeters of a solution of 1 gram of diphenylamine in 100 cc. of concentrated sulfuric acid, give a blue color if a trace of nitrate is present.

ing is made from sodium nitrate. This salt is hygroscopic, but a heavy graphite glaze produces a powder from it which is satisfactory under a variety of climatic conditions. Analyses of samples of granulated American blasting powder have shown that the compositions vary widely, sodium nitrate from 67.3 to 77.1 per cent, charcoal from 9.4 to 14.3 per cent, and sulfur from 22.9 to 8.6 per cent. Perhaps sodium nitrate 73, charcoal 11, and sulfur 16 may be taken as average values.

*Pellet powders,* made from sodium nitrate, are finding extensive use. These consist of cylindrical "pellets," 2 inches long, wrapped in paraffined paper cartridges, 1¼, 1⅜, 1½, 1¾, and 2 inches in diameter, which resemble cartridges of dynamite. The cartridges contain 2, 3, or 4 pellets which are perforated in the direction of their axis with a ⅜-inch hole for the insertion of a squib or fuse for firing.

**Ammonpulver**

Propellent powder made from ammonium nitrate is about as powerful as smokeless powder and has long had a limited use for military purposes, particularly in Germany and Austria. The Austrian army used Ammonpulver, among others, during the first World War, and it is possible that the powder is now, or may be at any time, in use.

Gäns of Hamburg in 1885 patented[21] a powder which contained no sulfur and was made from 40 to 45 per cent potassium nitrate, 35 to 38 per cent ammonium nitrate, and 14 to 22 per cent charcoal. This soon came into use under the name of *Amidpulver,* and was later improved by decreasing the proportion of potassium nitrate. A typical improved Amidpulver, made from potassium nitrate 14 per cent, ammonium nitrate 37 per cent, and charcoal 49 per cent, gives a flashless discharge when fired in a gun and only a moderate amount of smoke. Ammonpulver which contains no potassium nitrate—in a typical example ammonium nitrate 85 per cent and charcoal 15 per cent, or a similar mixture containing in addition a small amount of aromatic nitro compound—is flashless and gives at most only a thin bluish-gray smoke which disappears rapidly. Rusch[22] has published data

[21] Ger. Pat. 37,631.

[22] *Seewesen,* January, 1909, cited by Escales, "Ammonsalpetersprengstoffe," Leipzig, 1909, p. 217.

which show that the temperature of the gases from the burning of ammonpulver (ammonium nitrate 80 to 90 per cent, charcoal 20 to 10 per cent) is below 900°, and that the ballistic effect is approximately equal to that of ballistite containing one-third of its weight of nitroglycerin.

Ammonpulver has the advantages of being cheap, powerful, flashless, and smokeless. It is insensitive to shock and to friction, and is more difficult to ignite than black powder. In use it requires a strong igniter charge. It burns rapidly, and in gunnery is used in the form of single-perforated cylindrical grains usually of a diameter nearly equal to that of the space within the cartridge. It has the disadvantages that it is extremely hygroscopic and that it will not tolerate wide changes of temperature without injury. The charges must be enclosed in cartridges which are effectively sealed against the ingress of moisture from the air. Ammonium nitrate has a transition point at 32.1°. If Ammonpulver is warmed above this temperature, the ammonium nitrate which it contains undergoes a change of crystalline state; this results in the crumbling of the large powder grains and consequent high pressures and, perhaps, bursting of the gun if the charge is fired. At the present time Ammonpulver appears to be the only modification of black powder which has interesting possibilities as a military propellant.

## Other Related Propellent Explosives

*Guanidine nitrate powders* have not been exploited, but the present availability of guanidine derivatives from the cyanamide industry suggests possibilities. The salt is stable and non-hygroscopic, and is a flashless explosive—cooler indeed than ammonium nitrate. Escales[23] cites a German patent to Gäns[24] for a blasting powder made from potassium nitrate 40 to 60 per cent, guanidine nitrate 48 to 24 per cent, and charcoal 12 to 16 per cent.

Two other powders, now no longer used, are mentioned here as historically interesting examples of propellants made up in accordance with the same principle as black powder, namely, the principle of mixing an oxidizing salt with a combustible material.

*Raschig's white blasting powder* was made by dissolving 65 parts of sodium nitrate and 35 parts of sodium cresol sulfonate

[23] Escales, *op. cit.*, p. 225.
[24] Ger. Pat. 54,429.

together in water, running the solution in a thin stream onto a rotating and heated steel drum whereby the water was evaporated, and scraping the finished powder off from the other side of the drum. It was cheap, and easy and safe to make, but was hygroscopic. For use in mining, it was sold in waterproof paper cartridges.

*Poudre Brugère* was made by grinding together 54 parts of ammonium picrate and 46 parts of potassium nitrate in a black powder wheel mill, and pressing and granulating, etc., as in the manufacture of black powder. The hard grains were stable and non-hygroscopic. The powder was used at one time in military weapons. It was more powerful than black powder and gave less smoke.

# CHAPTER III

## PYROTECHNICS

The early history of pyrotechnics and the early history of black powder are the same narrative. Incendiary compositions containing saltpeter, and generally sulfur, mixed with combustible materials were used both for amusement and for purposes of war. They developed on the one hand into black powder, first used in crackers for making a noise and later in guns for throwing a projectile, and on the other into pyrotechnic devices. The available evidence indicates that fireworks probably developed first in the Far East, possibly in India earlier than in China, and that they were based upon various compositions of potassium nitrate, sulfur, and charcoal, with the addition of iron filings, coarse charcoal, and realgar ($As_2S_2$) to produce different visual effects. The nature of the composition and the state of subdivision of its ingredients determine the rate of burning and the appearance of the flame. In Chinese fire, coarse particles of hard-wood charcoal produce soft and lasting sparks; filings of cast iron produce bright and scintillating ones. The original Bengal lights were probably made more brilliant by the addition of realgar.

The manufacture of pyrotechnics from the Renaissance onward has been conducted, and still is practiced in certain places, as a household art or familiar craft. The artificer[1] needs patience and skill and ingenuity for his work. For large-scale factory production, the pyrotechnist has few problems in chemical engineering but many in the control of craftsmanship. His work, like that of the wood-carver or bookbinder, requires manual dexterity but transcends artistry and becomes art by the free play of the imagination for the production of beauty. He knows the kinds of effects, audible and visible, which he can get from his materials. He knows this as the graphic artist knows the appearance of his

[1] In the French language the word *artificier* means fireworks maker, and *artifice* means a pyrotechnic device.

colors. His problem is twofold: the esthetic one of combining these effects in a manner to produce a result which is pleasing, and the wholly practical one of contriving devices—and the means for the construction of devices—which shall produce these results. Like the graphic artist, he had but few colors at first, and he created designs with those which he had—lights, fountains, showers, Roman candles, rockets, etc. As new colors were discovered, he applied them to the production of better examples of the same or slightly modified designs. At the same time he introduced factory methods, devised improvements in the construction of his devices, better tools, faster and more powerful machinery, and learned to conduct his operations with greater safety and with vastly greater output, but the essential improvements in his products since the beginning of the seventeenth century have been largely because of the availability of new chemical materials.

### Development of Pyrotechnic Mixtures

The use of antimony sulfide, $Sb_2S_3$, designated in the early writings simply as antimony, along with the saltpeter, sulfur, and charcoal, which were the standard ingredients of all pyrotechnic compositions, appears to have been introduced in the early part of the seventeenth century. John Bate's "Book of Fireworks," 1635, containing information derived from "the noted Professors, as Mr. Malthus, Mr. Norton, and the French Authour, Des Récreations Mathématiques,"[2] mentions no mixtures which contain antimony. Typical of his mixtures are the following.

> *Compositions for Starres.* Take saltpeter one pound, brimstone half a pound, gunpowder foure ounces, this must be bound up in paper or little ragges, and afterwards primed.
> *Another receipt for Starres.* Take of saltpeter one pound, gunpowder and brimston of each halfe a pound; these must be mixed together, and of them make a paste, with a sufficient quantity of oil of peter (petroleum), or else of faire water; of this paste you shal make little balles, and roll them in drie gunpowder dust; then dry them, and keepe them for your occasions.[3]

The iron scale which John Bate used in certain of his rocket

[2] F. Malthus (François de Malthe), "Treatise of Artificial Fireworks," 1629; Robert Norton, "The Gunner," 1628.

[3] John Bate, "The Mysteries of Nature and Art," London, 1635, Second Part, p. 101.

THE
SECOND BOOKE
Teaching moſt plainly, and withall
moſt exactly, the compoſing of all
manner of Fire-works for Tryumph
and Recreation.

By IOHN BATE.

LONDON,
Printed by *Thomas Harper* for *Ralph Mab*.
1635.

FIGURE 21. Title Page of John Bate's "Book of Fireworks." A "green man," such as might walk at the head of a procession, is shown scattering sparks from a fire club. The construction of this device is described as follows: "To make . . . you must fill diverse canes open at both ends (and

compositions probably produced no brilliant sparks but only glowing globules of molten slag which gave the rocket a more luminous tail. Hanzelet Lorrain[4] in 1630 showed a more advanced knowledge of the art and gave every evidence of being acquainted with it by his own experience. He described several mixtures containing antimony sulfide and compositions, for balls of brilliant fire to be thrown from the hand, which contain orpiment ($As_2S_3$) and verdigris.

> *Stars of the only two compositions which are well approved.* Take of powder (gunpowder) four ounces, of saltpeter two ounces, of sulfur two ounces, of camphor half an ounce, of steel filings two *treseaux,* of white amber half an ounce, of antimony (sulfide) half an ounce, of (corrosive) sublimate half an ounce. For double the efficacy it is necessary to temper all these powders with gum *agragante* dissolved in brandy over hot cinders. When you see that the gum is well swollen and fully ready to mix with the said brandy, it is necessary forthwith to mix them in a mortar with the powder, the quicker the better, and then to cut up the resulting paste into pieces. These stars are very beautiful and very flowery. Note that it is necessary to put them to dry in a pastry or baking oven after the bread has been taken off of the hearth.
>
> *Second star composition.* Take of saltpeter in fine and dry flour ten ounces, of charcoal, of sulfur, of powder (gunpowder), of antimony (sulfide), and of camphor each two *treseaux.* Temper the whole with oil of turpentine, and make it into a powdery (mealy) paste which you will put into little cartridges; and you will load them in the same manner as rockets [that is, by pounding in the charge]. When you wish to use them, it is necessary to remove the paper wrapper and to cut them into pieces setting a little black match (*mèche d'estoupin*) in the middle (of each piece) through a little hole which you will pierce there.
>
> *How fire balls are made so white that one can scarcely look at them without being dazzled.* Take a pound of sulfur, three pounds of saltpeter, half a pound of gum arabic, four ounces of orpiment: grind all together, and mix well by hand,

[4] Hanzelet Lorrain, "La pyrotechnie," Pont à Mousson, 1630. The author's name is a pseudonym of Jean Appier.

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of a foot long, or more, or lesse, as you think fit) with a slow composition, and binde them upon a staffe of four or five foot long; prime them so that one being ended, another may begin: you may prime them with a stouple or match (prepared as before). Make an osier basket about it with a hole in the very top to fire it by, and it is done."

FIGURE 22. Seventeenth-Century Fireworks Display, Lorrain, 1630. Flaming swords, shields and pikes, wheel of fire, rockets, stars, candles, serpents, water fireworks. The sun and the moon which are pictured are presumably aerial bombs, and the dragons are probably dragon rockets running on ropes but may possibly be imaginative representations of serpents of fire. The picture is convincing evidence that many of the varieties of fireworks which are now used (in improved form) for display purposes were already in use three centuries ago.

> and moisten with brandy and make into a stiff paste into which you will mix half a pound of ground glass, or of crystal in small grains, not in powder, which you will pass through a screen or sieve. Then, mixing well with the said paste, you will form balls of it, of whatever size you please and as round as you can make them, and then you will let them dry. If you wish to have green fire, it is necessary merely to add a little verdigris to the composition. This is a very beautiful fire and thoroughly tested, and it needs no other primer to fire it than the end of a lighted match, for, as soon as the fire touches it, it inflames forthwith. It is beautiful in saluting a prince or nobleman to have such agreeable hand fire balls before setting off any other fireworks.[5]

Audot, whose little book[6] we take to be representative of the state of the art at the beginning of the nineteenth century, had a slightly larger arsenal of materials.

*Iron and steel filings.* "They give white and red sparks. It is necessary to choose those which are long and not rolled up, and to separate them from any dirt. They are passed through two sieves, in order to have two sizes, fine filings and coarse filings. Those of steel are in all respects to be preferred. It is easy to procure them from the artisans who work in iron and steel."

*Ground and filed cast iron.* "Cast iron is used in the fires which are designated by the name of *Chinese fire*. Two kinds, fine and coarse. The cast iron is ground in a cast iron mortar with a cast iron or steel pestle, and then sifted."

*Red copper filings.* "This gives greenish sparks."

*Zinc filings* "produce a beautiful blue color; it is a substance very difficult to file."

*Antimony* (sulfide) "gives a blue flame. It is ground up and passed through a screen of very fine silk."

*Yellow amber.* "Its color, when it burns, is yellow. It is used only for the fire of lances. It is very common in the drug trade. It ought to be ground and passed through a sieve."

*Lampblack.* "It gives a very red color to fire, and it gives rose in certain compositions."

*Yellow sand or gold powder.* "It is used in suns where it produces golden yellow rays. It is a reddish yellow sand mixed with

[5] Hanzelet Lorrain, *op. cit.*, pp. 256-258.

[6] Anon. (L.-E. Audot), "L'art de faire, à peu de frais, les feux d'artifice," Paris, 1818.

little brilliant scales. The paperers sell it under the name of gold powder. It is very common in Paris."[7]

Some of Audot's compositions are as follows:

*Common fire:* meal powder 16 parts, coarse and fine charcoal 5 parts.

*Chinese fire:* meal powder 16 parts, cast iron 6 parts.

*Brilliant fire:* meal powder 16 parts, steel filings 4 parts.

*Blue fire for cascades:* meal powder 16 parts, saltpeter 8, sulfur 12, and zinc filings 12 parts.

*Fixed star:* saltpeter 16 parts, sulfur 4, meal powder 4, and antimony (sulfide) 2 parts.

*Silver rain* for a turning sun or fire wheel: meal powder 16 parts, saltpeter 1, sulfur 1, steel filings 5 parts.

*Green fire* for the same: meal powder 16 parts, copper filings 3 parts.

*Chinese fire* for the same: meal powder 16 parts, saltpeter 8, fine charcoal 3, sulfur 3, fine and coarse cast iron 10 parts.

*Composition for lances. Yellow:* saltpeter 16 parts, meal powder 16, sulfur 4, amber 4, and colophony 3 parts. *Rose:* saltpeter 16 parts, lampblack 1, meal powder 3. *White:* saltpeter 16 parts, sulfur 8, meal powder 4. *Blue:* saltpeter 16 parts, antimony (sulfide) 8, very fine zinc filings 4. *Green:* saltpeter 16 parts, sulfur 6, verdigris 16, and antimony (sulfide) 6 parts.

*Bengal flame:* saltpeter 16 parts, sulfur 4, and antimony (sulfide) 2 parts. This mixture was to be lighted by quickmatch and burned in small earthenware pots for general illumination.[8]

The Ruggieri, father and son, contributed greatly to the development of fireworks by introducing new, and often very elaborate, pieces for public display and by introducing new materials into the compositions. They appear to have been among the first who attempted to modify the colors of flames by the addition of salts. The compositions which we have cited from Audot are similar to some of those which the elder Ruggieri undoubtedly used at an earlier time, and the younger Ruggieri, earlier than Audot's book, was using materials which Audot does not mention, in particular, copper sulfate and ammonium chloride for the green fire of the palm-tree set piece. The use of ammonium chloride was a definite advance, for the chloride helps to volatilize the copper and to produce a brighter color. But ammonium

[7] Audot, *op. cit.*, pp. 15-19.

[8] Audot, *op. cit.*, pp. 48, 49, 50, 52, 63, 64, 67.

chloride is somewhat hygroscopic and tends to cake, and it is now no longer used; indeed, the chloride is unnecessary in compositions which contain chlorate or perchlorate. In the Ruggieri "we have two pyrotechnists who can be considered to represent the best skill of France and Italy; in fact, it was Ruggieri whose arrival in France from Italy in or about 1735 marked the great advance in pyrotechny in the former country."[9] The elder Ruggieri conducted a fireworks display at Versailles in 1739. In 1743 he exhibited for the first time, at the Théâtre de la Comédie Italienne and before the King, the passage of fire from a moving to a fixed piece. "This ingenious contrivance at first astonished the scientists of the day, who said when it was explained to them that nothing could be more simple and that any one could have done it at once."[10] In 1749 he visited England to conduct, with Sarti, a fireworks display in Green Park in celebration of the peace of Aix-la-Chapelle. The younger Ruggieri conducted many public pyrotechnic exhibitions in France during the years 1800-1820, and wrote a treatise on fireworks which was published both in French and in German.

Potassium chlorate had been discovered, or at least prepared in a state of purity, by Berthollet in 1786. It had been tried unsuccessfully and with disastrous results in gunpowder. Forty years elapsed before it began to be used in pyrotechnic mixtures, where, with appropriate salts to color the flame, it yields the brilliant and many-colored lights which are now familiar to us. At present it is being superseded for certain purposes by the safer perchlorate.

James Cutbush, acting professor of chemistry and mineralogy at West Point, in his posthumous "System of Pyrotechny," 1825, tells[11] of the detonation of various chlorate mixtures and of their use for the artificial production of fire. "Besides the use of nitre in pyrotechnical compositions, as it forms an essential part of all

[9] A. St. H. Brock, "Pyrotechnics: The History and Art of Fireworks Making," London, 1922. This is a scholarly and handsome book, bountifully illustrated, which contains excellent accounts both of the history of fireworks and of present manufacturing practice. The author comes from several generations of fireworks makers.

[10] Quoted by Brock, *op. cit.*, p. 124.

[11] James Cutbush, "A System of Pyrotechny, Comprehending the Theory and Practice, with the Application of Chemistry; Designed for Exhibition and for War," Philadelphia, 1825, p. 22.

of them, there is another salt . . . that affords a variety of amusing experiments. This salt is the hyperoxymuriate or chlorate of potassa. Although it has neither been used for fire-works on an extensive scale, nor does it enter into any of the compositions usually made for exhibition, yet its effect is not the less amusing." At a later place Cutbush says: "M. Ruggieri is of opinion, that chlorate, or hyperoxymuriate of potassa may be employed with advantage in the composition of rockets, but we have not heard that it has been used. It is more powerful in its effects, and probably for this reason he recommended it. This salt, mixed with other substances, will produce the *green fire* of the palm-tree, in imitation of the Russian fire."[12]

Ruggieri's Russian fire, as his son later described it, consisted of crystallized copper acetate 4 parts, copper sulfate 2 parts, and ammonium chloride 1 part,[13] all finely pulverized and mixed with alcohol, and placed upon cotton wick attached to spikes upon the thin metal pieces which were the leaves of the palm tree. The resulting display would not be impressive according to modern standards.

Cutbush also knew how to color the flame, for he says:

> We are of opinion, that many of the nitrates might be advantageously employed in the manufacture of fire works. Some, as nitrate of strontian, communicate a red color to flame, as the flame of alcohol. Nitrate of lime also might be used. . . . Muriate of strontian, mixed with alcohol, or spirit of wine, will give a carmine-red flame. For this experiment, one part of the muriate is added to three or four parts of alcohol. Muriate of lime produces, with alcohol, an orange-coloured flame. Nitrate of copper produces an emerald-green flame. Common salt and nitre, with alcohol, give a yellow flame.[14]

According to Brock, the use of chlorate in pyrotechnic mixtures, initiating the modern epoch in the art, first occurred about 1830. Lieut. Hippert of the Belgian artillery published at Bruxelles in 1836 a French translation, "Pyrotechnie raisonnée," of a work by Prussian artillery Captain Moritz Meyer in which one chapter is devoted to colored fires, and listed several com-

[12] Cutbush, *op. cit.*, p. 77.

[13] Ruggieri, "Handbüchlein der Lustfeuerwerkerei," second edition, Quedlinburg and Leipzig, 1845, p. 142.

[14] Cutbush, *op. cit.*, pp. 8 and 20.

positions which contain potassium chlorate. Meyer states, incidentally, that the English at that time used colored rockets for signaling at sea and were able to produce ten distinguishable shades. His descriptions of his compositions give one reason to suspect that he had had little experience with them himself. The first, a mixture of potassium chlorate and sugar, burns, he says, with a red light; but the color is actually a bluish white.

> A powder which burns with a green flame is obtained by the addition of nitrate of baryta to chlorate of potash, nitrate of potash, acetate of copper. A white flame is made by the addition of sulfide of antimony, sulfide of arsenic, camphor. Red by the mixture of lampblack, coal, bone ash, mineral oxide of iron, nitrate of strontia, pumice stone, mica, oxide of cobalt. Blue with ivory, bismuth, alum, zinc, copper sulfate purified of its sea water [*sic*]. Yellow by amber, carbonate of soda, sulfate of soda, cinnabar. It is necessary in order to make the colors come out well to animate the combustion by adding chlorate of potash.[15]

Although Meyer's formulas are somewhat incoherent, they represent a definite advance. Equally significant with the use of chlorate is his use of the nitrates of strontium and barium.

The second German edition of Ruggieri's book (we have not seen the first) contains a *Nachtrag* or supplement which lists nine compositions,[16] of which four contain *Kali oxym.* or potassium chlorate. These are: (1) for red fire, strontium nitrate 24 parts, sulfur 3, fine charcoal 1, and potassium chlorate 5; (2) for green fire, barium carbonate 20 parts, sulfur 5, and potassium chlorate 8 parts; (3) for green stars, barium carbonate 20 parts, sulfur 5, and potassium chlorate 9 parts; and (4) for red lances, strontium carbonate 24 parts, sulfur 4, charcoal 1, and potassium chlorate 4 parts. Ruggieri says:

> The most important factor in the preparation of these compositions is the fine grinding and careful mixing of the several materials. Only when this is done is a beautiful flame to be expected. And it is further to be noted that the potassium chlorate, which occurs in certain of the compositions, is to be wetted with spirit for the grinding in order to avoid an explosion.

[15] Brock, *op. cit.*, pp. 145, 146.
[16] Ruggieri, *op. cit.*, pp. 147, 148.

The chlorate compositions recommended by Ruggieri would undoubtedly give good colors, but are not altogether safe and would probably explode if pounded into their cases. They could be loaded with safety in an hydraulic press, and would probably not explode if tamped carefully by hand.

F. M. Chertier, whose book "Nouvelles recherches sur les feux d'artifice" was published at Paris in 1854, devotes most of his attention to the subject of color, so successfully that, although new materials have come into use since his time, Brock says that "there can be no doubt that Chertier stands alone in the literature of pyrotechny and as a pioneer in the modern development of the art."[17] Tessier, in his "Chimie pyrotechnique ou traité pratique des feux colores," first edition, Paris, 1859, second edition 1883, discusses the effect of individual chemicals upon the colors of flames and gives excellent formulas for chlorate and for non-chlorate compositions which correspond closely to present practice. He used sulfur in many but not in all of his chlorate mixtures. Pyrotechnists in France, with whom the present writer talked during the first World War, considered Tessier's book at that time to be the best existing work on the subject of colored fires—and this in spite of the fact that its author knew nothing of the use of magnesium and aluminum. The spectroscopic study of the colors produced by pure chemicals, and of the colors of pyrotechnic devices which are best suited for particular effects, is the latest of current developments.

Chlorate mixtures which contain sulfur give brighter flames than those which lack it, and such mixtures are still used occasionally in spite of their dangerous properties. The present tendency, however, is toward chlorate mixtures which contain no sulfur, or toward potassium nitrate mixtures (for stars, etc.) which contain sulfur but no chlorate, or toward nitrates, such as those of strontium and barium, which supply both color for the flame and oxygen for the combustion and are used with magnesium or aluminum to impart brilliancy. Magnesium was first used for pyrotechnic purposes about 1865 and aluminum about 1894, both of them for the production of dazzling white light. These metals were used in the compositions of colored airplane

[17] Brock, *op. cit.*, p. 147. Chertier also published a pamphlet on colored fires nearly thirty years earlier than the above-mentioned book.

flares during the first World War, but their use in the colored fires of general pyrotechny is largely a later development.

Tessier introduced the use of cryolite ($AlNa_3F_6$) for the yellow coloring of stars, lances, and Bengal lights. In his second edition he includes a chapter on the small pyrotechnic pieces which are known as Japanese fireworks, giving formulas for them, and another on the picrates, which he studied extensively. The picrates of sodium, potassium, and ammonium crystallize in the anhydrous condition. Those of barium, strontium, calcium, magnesium, zinc, iron, and copper are hygroscopic and contain considerable water of crystallization which makes them unfit for use in pyrotechnic compositions. Lead picrate, with 1 $H_2O$, detonates from fire and from shock, and its use in caps and primers was patented in France in 1872. Potassium and sodium picrate deflagrate from flame, retaining that property when mixed with other substances. Ammonium picrate detonates from fire and from shock when in contact with potassium chlorate or lead nitrate, but in the absence of these substances it has the special advantage for colored fires that the mixtures give but little smoke and this without offensive odor. Tessier recommends ammonium picrate compositions for producing colored lights in the theater and in other places where smoke might be objectionable. "Indoor fireworks" have been displaced in the theater by electric lighting devices, but are still used for certain purposes. Tessier's formulas, which are excellent, are described later in the section on picrate compositions.

## Colored Lights

Colored light compositions are used in the form of a loose powder, or are tamped into paper tubes in torches for political parades, for highway warnings, and for railway and marine signals, in Bengal lights, in airplane flares, and in lances for set pieces, or are prepared in the form of compact pellets as stars for Roman candles, rockets, and aerial bombs, or as stars to be shot from a special pistol for signaling.

Colored fire compositions intended for burning in conical heaps or in trains are sometimes sold in paper bags but more commonly in boxes, usually cylindrical, of pasteboard, turned wood, or tinned iron. The mixtures are frequently burned in the boxes in

which they are sold. Compositions which contain no chlorate (or perchlorate) are the oldest, and are still used where the most brilliant colors are not necessary.

| | White | | | | | Red | Pink | | Yellow |
|---|---|---|---|---|---|---|---|---|---|
| Potassium nitrate | 5 | 3 | 32 | 8 | 14 | .. | 12 | 14 | .. |
| Sulfur | 2 | 1 | 15 | 2 | 4 | 5 | 5 | 4 | 3 |
| Strontium nitrate | .. | .. | .. | .. | .. | 18 | 48 | 36 | .. |
| Barium nitrate | .. | .. | .. | .. | .. | .. | .. | .. | 36 |
| Sodium oxalate | .. | .. | .. | .. | .. | .. | .. | .. | 6 |
| Antimony metal | .. | 1 | 12 | .. | .. | .. | .. | .. | .. |
| Antimony sulfide | 1 | 1 | .. | .. | .. | .. | .. | .. | .. |
| Realgar | .. | .. | .. | 1 | 5 | .. | .. | .. | .. |
| Minium | .. | .. | 10 | .. | .. | .. | .. | .. | .. |
| Lampblack | .. | .. | .. | .. | .. | 1 | .. | .. | .. |
| Charcoal | .. | .. | .. | .. | .. | .. | 4 | 1 | .. |
| Red gum | .. | .. | .. | .. | .. | .. | .. | 4 | 5 |
| Dextrin | .. | .. | 1 | .. | .. | .. | .. | 1 | .. |

The chlorate compositions listed below, which contain no sulfur, burn rapidly with brilliant colors and have been recommended for indoor and theatrical uses.

| | White | Red | Yellow | Green |
|---|---|---|---|---|
| Potassium chlorate | 12 | 1 | 6 | 2 |
| Potassium nitrate | 4 | .. | 6 | .. |
| Strontium nitrate | .. | 4 | .. | .. |
| Barium nitrate | .. | .. | .. | 1 |
| Barium carbonate | 1 | .. | .. | .. |
| Sodium oxalate | .. | .. | 5 | .. |
| Cane sugar | 4 | .. | .. | 1 |
| Stearine | 1 | .. | .. | .. |
| Shellac | .. | 1 | 3 | .. |

The following are brilliant, somewhat slower burning, and suitable for outdoor use and general illumination. The smokes from the compositions which contain calomel and Paris green are poisonous. In mixing Paris green, care must be exercised not to inhale the dust.

| | Red | | | Green | | Blue | | |
|---|---|---|---|---|---|---|---|---|
| Potassium chlorate | 10 | 4 | 8 | 4 | 4 | 6 | 8 | 16 |
| Strontium nitrate | 40 | 10 | 16 | .. | .. | .. | .. | .. |
| Barium nitrate | .. | .. | .. | 8 | 8 | 4 | .. | 14 |
| Paris green | .. | .. | .. | .. | .. | 4 | .. | 12 |
| Shellac | .. | .. | 3 | .. | 3 | .. | .. | 1 |
| Stearine | .. | .. | .. | .. | .. | 1 | .. | 2 |
| Red gum | 6 | 3 | .. | 2 | .. | .. | .. | .. |
| Calomel | .. | .. | .. | .. | .. | .. | 6 | 2 |
| Sal ammoniac | .. | .. | .. | 1 | .. | 1 | .. | .. |
| Copper ammonium chloride | .. | .. | .. | .. | .. | .. | 2 | .. |
| Fine sawdust | 6 | .. | .. | .. | .. | .. | .. | .. |
| Rosin | .. | 1 | .. | .. | .. | .. | .. | .. |
| Lampblack | 1 | 1 | .. | .. | .. | .. | .. | .. |
| Milk sugar | .. | .. | .. | .. | .. | .. | 3 | .. |

**Railway Fusees** (Truck Signal Lights)

Motor trucks are required by law to be equipped with red signal lights for use as a warning in case an accident causes them to be stopped on the road at night without the use of their electric lights. Similar lights are used for signaling on the railways. The obvious requirement is that the signal should burn conspicuously and for a long time. A. F. Clark recommends a mixture of:

| | Parts |
|---|---|
| Strontium nitrate (100 mesh) | 132 |
| Potassium perchlorate (200 mesh) | 15 |
| Prepared maple sawdust (20 mesh) | 20 |
| Wood flour (200 mesh) | 1 |
| Sulfur (200 mesh) | 25 |

The prepared maple sawdust is made by cooking with miner's wax, 10 pounds of sawdust to 1 ounce of wax, in a steam-jacketed kettle. The mixture is tamped dry into a paper tube, 7/8 inch in external diameter, 1/32 inch wall, and burns at the rate of about 1 inch per minute. The fusee is supplied at its base with a pointed piece of wood or iron for setting it up in the ground, and it burns best when set at an angle of about 45°. In order to insure certain ignition, the top of the charge is covered with a primer or *starting fire,* loaded while moistened with

alcohol, which consists of potassium chlorate 16 parts, barium chlorate 8, red gum (gum yacca) 4, and powdered charcoal 1. This is covered with a piece of paper on which is painted a *scratch mixture* similar to that which composes the head of a safety match. The top of the fusee is supplied with a cylindrical paper cap, the end of which is coated with a material similar to that with which the striking surface on the sides of a box of safety matches is coated. To light the fusee, the cap is removed and inverted, and its end or bottom is scratched against the mixture on the top of the fusee.

Weingart[18] recommends the first four of the following compositions for railway fusees; Faber[19] reports the fifth. Weingart's mixtures are to be moistened with kerosene before they are tamped into the tubes.

| | | | | | |
|---|---|---|---|---|---|
| Potassium chlorate | .. | .. | .. | .. | 12 |
| Potassium perchlorate | .. | .. | .. | 5 | .. |
| Strontium nitrate | 48 | 36 | 16 | 36 | 72 |
| Saltpeter | 12 | 14 | 4 | .. | .. |
| Sulfur | 5 | 4 | 5 | 5 | 10 |
| Fine charcoal | 4 | 1 | 1 | .. | .. |
| Red gum | 10 | 4 | .. | .. | 4 |
| Dextrin | .. | 1 | .. | .. | .. |
| Sawdust | .. | .. | .. | 2 | .. |
| Sawdust and grease | .. | .. | .. | .. | 4 |
| Calcium carbonate | .. | .. | .. | .. | 1 |

## Scratch Mixture

Typical scratch mixtures are the pair: (*A*) potassium chlorate 6, antimony sulfide 2, glue 1; and (*B*) powdered pyrolusite ($MnO_2$) 8, red phosphorus 10, glue 3, recommended by Weingart; and the pair: (*A*) potassium chlorate 86, antimony sulfide 52, dextrin 35; and (*B*) red phosphorus 9, fine sand 5, dextrin 4, used with gum arabic as a binder, and recommended by A. F. Clark.

## Marine Signals

Other interesting signal lights, reported by Faber,[20] are as follows.

[18] Weingart, "Dictionary and Manual of Fireworks," Boston, 1937, p. 61.
[19] Faber, "Military Pyrotechnics," 3 vols., Washington, 1919, Vol. I, p. 189.
[20] *Loc. cit.*

| | Marine Flare Torch | Pilot's Blue Light |
|---|---|---|
| Barium nitrate | 16 | .. |
| Potassium nitrate | 8 | .. |
| Potassium chlorate | .. | 46 |
| Strontium carbonate | 1 | .. |
| Copper oxychloride | .. | 32 |
| Sulfur | 2 | 28 |
| Red gum | 2 | .. |
| Shellac | .. | 48 |
| Calomel | .. | 3 |

## Parade Torches

Parade torches are made in various colors; they are of better quality than railway fusees, burn with a deeper color and a brighter light, and are generally made with more expensive compositions. Below are a few typical examples. Parade torches are

| | Red | | | Green | | Purple | Amber | Blue |
|---|---|---|---|---|---|---|---|---|
| Strontium nitrate | 16 | 5 | 9 | .. | .. | 7 | 36 | .. |
| Barium nitrate | .. | .. | .. | 40 | 30 | .. | .. | .. |
| Potassium chlorate | 8 | 1 | .. | 11 | .. | .. | .. | .. |
| Potassium perchlorate | .. | .. | 2 | .. | 6 | 9 | 10 | 5 |
| Sodium oxalate | .. | .. | .. | .. | .. | .. | 8 | .. |
| Cupric oxide | .. | .. | .. | .. | .. | 6 | .. | .. |
| Paris green | .. | .. | .. | .. | .. | .. | .. | 2 |
| Sal ammoniac | .. | .. | .. | 1 | .. | .. | .. | .. |
| Calomel | .. | .. | .. | .. | .. | 3 | .. | 1 |
| Sulfur | .. | .. | 2 | .. | 3 | 5 | 3 | .. |
| K.D. gum | .. | .. | .. | 6 | 2 | .. | .. | .. |
| Shellac | 3 | .. | .. | .. | .. | .. | 5 | .. |
| Red gum | .. | 1 | 1 | .. | .. | .. | .. | .. |
| Dextrin | .. | .. | .. | .. | .. | .. | .. | 1 |

equipped with wooden handles at the lower ends, and are sealed at their upper ends with a piece of cloth or paper, pasted on, through which a hole has been punched into the composition to a depth of about 1 inch—and through this a piece of *black match*[21]

[21] The match, prepared by dipping a few strands of cotton twine, twisted together, into a paste of meal powder and allowing to dry while stretched on a frame, is called *black match* by the pyrotechnists. When this is enclosed in a paper tube, it burns almost instantaneously and is then known as *quickmatch*. Such *quickmatch* is used for communicating fire in set pieces, Catherine wheels, etc.

has been inserted and fixed in place by a blob of paste of meal powder with gum-arabic water.

## Aluminum and Magnesium Flares

When barium and strontium nitrates are used in colored lights, these substances serve the twofold purpose of coloring the flame and of supplying oxygen for its maintenance. The materials which combine with the oxygen to yield the flame, in the compositions which have been described, have been sulfur and carbonaceous matter. If, now, part or all of these materials is substituted by magnesium or aluminum powder or flakes, the resulting composition is one which burns with an intensely bright light. A mixture of potassium perchlorate 7 parts, mixed aluminum powder and flakes 5 parts, and powdered sulfur 2 parts burns with a brilliant light having a lilac cast. A balanced mixture of barium and strontium nitrates, that is, of green and red, gives a light which is practically white. Such lights are used in parade torches and signals, but are so bright as to be trying to the eyes. They find important use in aviation for signaling and for illuminating landing fields and military objectives.

Magnesium is attacked fairly rapidly by moisture, and pyrotechnic mixtures containing this metal do not keep well unless the particles of magnesium are first coated with a protecting layer of linseed oil or similar material. Aluminum does not have the same defect and is more widely used. An excellent magnesium light, suitable for illumination, is described in a patent recently granted to George J. Schladt.[22] It consists of a mixture of 36 to 40 per cent barium nitrate, 6 to 8 per cent strontium nitrate, 50 to 54 per cent flake magnesium coated with linseed oil, and 1 to 4 per cent of a mixture of linseed and castor oils.

The airplane wing-tip flares which were used for signaling during the first World War are good examples[23] of aluminum compositions. They were loaded in cylindrical paper cases 4¼ inches in length and 1⅝ inches in internal diameter. The white light composition consisted of 77 parts of barium nitrate, 13 of flake aluminum, and 5 of sulfur intimately mixed and secured by a binder of shellac, and burned in the cases mentioned, for 1

[22] U. S. Pat. 2,149,314, March 7, 1939.

[23] Faber, *op. cit.*, Vol. 2, pp. 223, 225-227.

minute with an illumination of 22,000 candlepower. The red light was made from 24 parts of strontium nitrate, 6 of flake aluminum, and 6 of sulfur with a shellac binder and burned for 1 minute with an illumination of 12,000 to 15,000 candlepower. The compositions were loaded into the cases by means of a pneumatic press, and filled them to within 5/16 inch of the top. The charge was then covered with a ⅛-inch layer of starting fire or *first fire composition*, made from saltpeter 6 parts, sulfur 4, and charcoal 1, dampened with a solution of shellac in alcohol, and this, when the device was used, was fired by an electric squib.

## Lances

Lances are paper tubes, generally thin and of light construction, say, ¼ to ⅜ inch in diameter and 2 to 3½ inches long, filled with colored fire composition, loaded by tamping, not by ramming, and are used in set pieces, attached to wooden frameworks, to outline the figure of a temple or palace, to represent a flag, to spell words, etc. When set up, they are connected by quickmatch (black match in a paper tube) and are thus lighted as nearly simultaneously as may be. They are often charged in such manner as to burn with a succession of color, in which event the order of loading the various colors becomes important. Green should not be next to white, for there is not sufficient contrast. And green should not burn after red, for the color of the barium flame appears to one who has been watching the flame of strontium to be a light and uninteresting blue. The order of loading (the reverse of the order of burning) is generally white, blue (or yellow or violet) green, red, white. In the tables on page 70 a number of lance compositions are listed, illustrative of the various types and corresponding to considerable differences in cost of manufacture.

## Picrate Compositions

Ammonium picrate is used in the so-called indoor fireworks which burn with but little smoke and without the production of objectionable odor. On page 71 some of the compositions recommended by Tessier[24] for Bengal lights are tabulated.

[24] *Op. cit.*, second edition, pp. 383-396.

| | | | | | | |
|---|---|---|---|---|---|---|
| WHITE | Potassium nitrate | 33 | 5 | 9 | 8 | 11 |
| | Antimony sulfide | 5 | .. | 2 | .. | 1 |
| | Antimony metal | .. | 1 | .. | .. | 3 |
| | Realgar | .. | .. | .. | 1 | .. |
| | Sulfur | 11 | 2 | 1 | 2 | 3 |
| | Meal powder | 2 | 1 | .. | .. | .. |
| RED | Potassium chlorate | | | 10 | 6 | 36 |
| | Strontium nitrate | | | .. | .. | 54 |
| | Strontium carbonate | | | 3 | 2 | .. |
| | Sulfur | | | .. | .. | 13 |
| | Lampblack | | | .. | .. | 2 |
| | Shellac | | | 2 | .. | 12 |
| | Paraffin | | | .. | 1 | .. |
| YELLOW | Potassium perchlorate | | .. | .. | .. | 24 |
| | Potassium chlorate | | 8 | 4 | 4 | .. |
| | Barium nitrate | | 1 | .. | 22 | .. |
| | Sodium oxalate | | .. | 2 | .. | 8 |
| | Sodium bicarbonate | | 2 | .. | .. | .. |
| | Cryolite | | .. | .. | 2 | .. |
| | Sulfur | | 4 | .. | 5 | .. |
| | Lampblack | | .. | .. | 1 | .. |
| | Shellac | | .. | 1 | .. | 3 |
| GREEN | Potassium chlorate | | .. | .. | 7 | .. |
| | Barium nitrate | | 12 | 4 | 7 | .. |
| | Barium chlorate | | 9 | 5 | .. | 6 |
| | Lampblack | | 1 | .. | .. | .. |
| | Shellac | | 10 | 1 | 2 | 1 |
| BLUE | Potassium perchlorate | | | 16 | .. | .. |
| | Potassium chlorate | | | .. | 32 | 5 |
| | Copper oxychloride | | | .. | .. | 2 |
| | Paris green | | | 6 | 10 | .. |
| | Calomel | | | 1 | 6 | .. |
| | Shellac | | | 1 | .. | 1 |
| | Stearine | | | .. | 3 | .. |
| LILAC | Potassium chlorate | | | | | 26 |
| | Strontium sulfate | | | | | 10 |
| | Basic copper sulfate | | | | | 6 |
| | Lead nitrate | | | | | 5 |
| | Sulfur | | | | | 4 |
| | Shellac | | | | | 1 |
| | Stearine | | | | | 1 |
| VIOLET | Potassium chlorate | | | | | 25 |
| | Strontium sulfate | | | | | 20 |
| | Basic copper sulfate | | | | | 1 |
| | Sulfur | | | | | 20 |

To be burned without compression, in the open, in trains or in heaps:

| | Red | | Green | | Aurora | Yellow | White |
|---|---|---|---|---|---|---|---|
| Ammonium picrate. | | 10 | | | 10 | 20 | 5 |
| Strontium nitrate.. | 25 | 40 | | | 31 | 12 | .. |
| Barium nitrate..... | | | 32 | 25 | | 58 | 30 |
| Cryolite.......... | | | | | | 7 | .. |
| Antimony metal... | | | | | | .. | 5 |
| Lampblack........ | | | | | | 4 | 1 |
| Paraffin........... | | | | | | 2 | 1 |

To be compressed in paper cartridges, 25-30 mm. internal diameter, to be burned in a horizontal position in order that the residue may not interfere with the burning:

| | Red | | Green | | | Aurora | Yellow | | White | |
|---|---|---|---|---|---|---|---|---|---|---|
| Ammonium picrate....... | 1 | 20 | 5 | 5 | 11 | 20 | 20 | 24 | 6 | 5 |
| Strontium nitrate........ | 1 | 60 | .. | .. | .. | 60 | 10 | 3 | .. | .. |
| Barium nitrate.......... | .. | .. | 6 | 28 | 36 | .. | 60 | 20 | 4 | 30 |
| Cryolite................ | .. | .. | .. | .. | .. | 7 | 7 | 4 | .. | .. |
| Calcium fluoride......... | .. | 7 | .. | .. | .. | .. | .. | .. | .. | .. |
| Antimony metal......... | .. | .. | .. | .. | .. | .. | .. | .. | .. | 4 |
| Antimony sulfide........ | .. | .. | .. | .. | .. | .. | .. | .. | 3 | 1 |
| Lampblack.............. | .. | 4 | .. | 1 | 1 | 4 | 4 | .. | .. | 1 |
| Paraffin................ | .. | 2 | .. | 1 | 1 | 2 | 2 | .. | .. | 1 |

Picric acid added in small quantities to colors deepens them and increases their brilliancy without making them burn much faster. Stars containing picric acid ought not to be used in aerial shells, for they are likely to detonate either from the shock of setback or later from being ignited in a confined space. Mixtures which contain picric acid along with potassium chlorate or salts of heavy metals are liable to detonate from shock.

Weingart[25] lists two "smokeless tableau" fires which contain picric acid, as follows:

[25] *Op. cit.*, p. 60.

| | Red | Green |
|---|---|---|
| Strontium nitrate | 8 | .. |
| Barium nitrate | .. | 4 |
| Picric acid | 5 | 2 |
| Charcoal | 2 | 1 |
| Shellac | 1 | .. |

The picric acid is to be dissolved in boiling water, the strontium or barium nitrate added, the mixture stirred until cold, and the solid matter collected and dried. The same author[26] gives picric acid compositions for stars, "not suitable for shells," as follows:

| | Red | | Green |
|---|---|---|---|
| Strontium nitrate | 8 | .. | .. |
| Strontium carbonate | .. | 3 | .. |
| Barium chlorate | .. | .. | 12 |
| Potassium chlorate | 4 | 10 | 8 |
| Picric acid | 1.5 | 1.5 | 2 |
| Calomel | .. | .. | 6 |
| Shellac | 1.5 | 0.75 | 2 |
| Fine charcoal | 1 | 1 | .. |
| Lampblack | .. | .. | 1.5 |
| Dextrin | 0.5 | 0.75 | 0.5 |

### Picrate Whistles

An intimate mixture of finely powdered dry potassium picrate and potassium nitrate, in the proportion about 60/40, rammed tightly into paper, or better, bamboo tubes from ¼ to ¾ inch in diameter, burns with a loud whistling sound. The mixture is dangerous, exploding from shock, and cannot be used safely in aerial shells. Whistling rockets are made by attaching a tube of the mixture to the outside of the case in such manner that it burns, and whistles, during the flight—or by loading a small tube, say ¼ inch in diameter and 2½ inches long, into the head of the rocket to produce a whistle when the rocket bursts. The mixture

[26] *Op. cit.*, pp. 114, 115.

is used in whistling firecrackers, "musical salutes," "whistling whizzers," "whistling tornados," etc. The effect of a whistle as an accompaniment to a change in the appearance of a burning wheel is amusing. Whistles are perhaps most effective when six or eight of them, varying in size from the small to the large, are fired in series, the smallest caliber and the highest pitch being first.

### Non-Picrate Whistles

Non-picrate whistles, made from a mixture of 1 part powdered gallic acid and 3 parts potassium chlorate, are considered to be safer than those which contain picrate. The mixture is charged into a ½-inch case, 5/16 inch in internal diameter. The case is loaded on a 1-inch spindle, and the finished whistle has a 1-inch length of empty tube which is necessary for the production of the sound. Whistles of this sort, with charges of a chlorate or perchlorate explosive at their ends, are used in "chasers," "whizzers," etc., which scoot along the ground while whistling and finally explode with a loud report.

### Rockets

The principle of the rocket and the details of its design were worked out at an early date. Improvements have been in the methods of manufacture and in the development of more brilliant and more spectacular devices to load in the rocket head for display purposes. When rockets are made by hand, the present practice is still very much like that which is indicated by Figure 23. The paper casing is mounted on a spindle shaped to form the long conical cavity on the surface of which the propelling charge will start to burn. The composition is rammed into the space surrounding the spindle by means of perforated ram rods or *drifts* pounded by a mallet. The base of the rocket is no longer choked by crimping, but is choked by a perforated plug of clay. The clay, dried from water and moistened lightly with crankcase oil, is pounded or pressed into place, and forms a hard and stable mass. The tubular paper cases of rockets, *gerbs*,[27] etc., are now often made by machinery, and the compositions are loaded into them automatically or semi-automatically and pressed by hydraulic presses.

[27] Pronounced *jurbs*.

John Bate and Hanzelet Lorrain understood that the heavier rockets require compositions which burn more slowly.

> It is necessary to have compositions according to the greatness or the littleness of the rockets, for that which is proper for the little ones is too violent for the large—because the fire, being lighted in a large tube, lights a composition of great amplitude, and burns a great quantity of material,

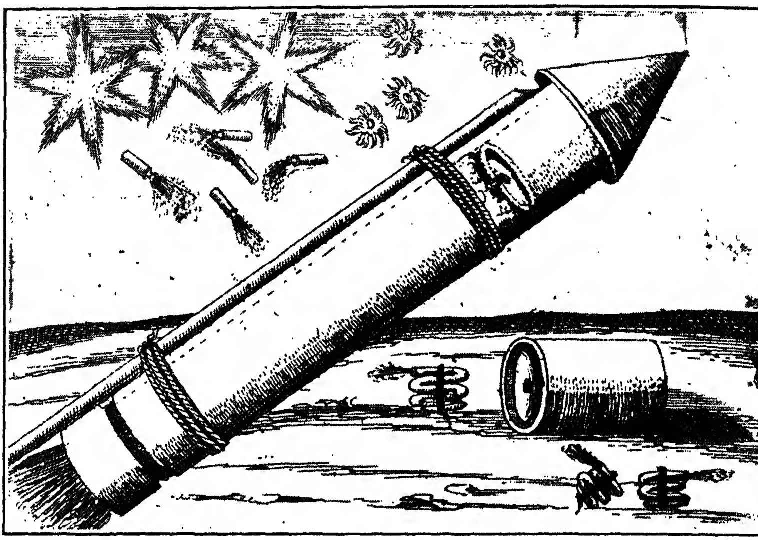


FIGURE 23. Rocket, Lorrain, 1630. Substantially as rockets are made today. After the propelling charge has burned completely and the rocket has reached the height of its flight, the fire reaches the charge in the head which bursts and throws out large and small stars, serpents and grasshoppers, or English firecrackers. The container, which is loaded into the head of the rocket, is shown separately with several grasshoppers in the lower right-hand corner of the picture.

> and no geometric proportionality applies. Rockets intended to contain an ounce or an ounce and a half should have the following for their compositions.
>
> Take of fine powder (gunpowder) passed through a screen or very fine sieve four ounces, of soft charcoal one ounce, and mix them well together.[28]
>
> *Otherwise.* Of powder sieved and screened as above one pound, of saltpeter one ounce and a half, of soft charcoal

[28] The charcoal makes the powder burn more slowly, and produces a trail of sparks when the rocket is fired.

one ounce and a half. It does not matter what charcoal it is; that of light wood is best, particularly of wood of the vine.

*For rockets weighing two ounces.* Take of the above-said powder four ounces and a half, of saltpeter one ounce.

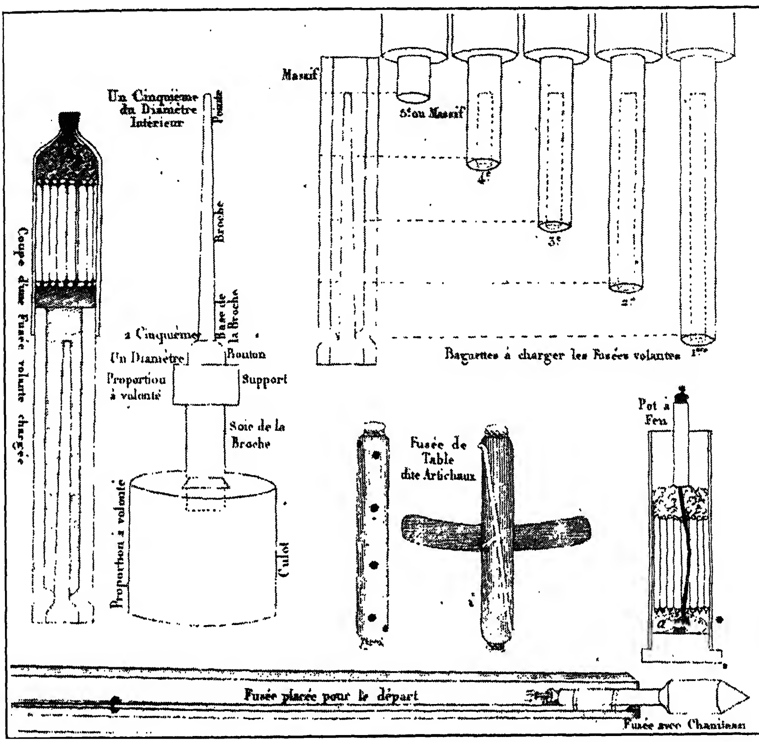



FIGURE 24. Details of Construction of Rocket and of Other Pieces, Audot, 1818. The rocket case, already crimped or constricted, is placed upon the spindle (*broche*); the first portion of the propelling charge is introduced and pounded firmly into place by means of a mallet and the longest of the *drifts* pictured in the upper right-hand corner; another portion of the charge is introduced, a shorter drift is used for tamping it, and so on until the case is charged as shown at the extreme left. A tourbillion (table rocket or artichoke) and a mine charged with serpents of fire are also shown.

*Otherwise for the same weight.* Take powder two ounces, of soft charcoal half an ounce.

*Composition for rockets weighing from 4 to 8 ounces.* Take powder as above seventeen ounces, of saltpeter four ounces, of soft charcoal four ounces.

*Otherwise and very good.* Of saltpeter ten ounces, of sulfur one ounce, of powder three ounces and a half, of charcoal three ounces and a half.

*To make them go up more suddenly.* Take of powder ten ounces, of saltpeter three ounces and a half, of sulfur one ounce, of charcoal three ounces and a half.

*For rockets weighing one pound.* Take of powder one pound, of soft charcoal two ounces, and of sulfur one ounce.

*Otherwise.* Of saltpeter one pound four ounces, of sulfur two ounces, of soft charcoal five ounces and a half.

*For rockets weighing three pounds.* Of saltpeter 30 ounces, of charcoal 11 ounces, of sulfur 7 ounces and a half.

*For rockets weighing four, five, six, and seven pounds.* Of soft charcoal ten pounds, of sulfur four pounds and a half, of saltpeter thirty one pounds.[29]

Present practice is illustrated by the specifications tabulated below for 1-ounce, 3-ounce, and 6-pound rockets as now manufactured by an American fireworks company. The diameter of

| | | Ounce | Ounce | Pound |
|---|---|---|---|---|
| Size. | | 1 | 3 | 6 |
| Composition of charge | Saltpeter | 36 | 35 | 30 |
| | Sulfur | 6 | 5 | 5 |
| | No. 3 charcoal | .. | 5 | 12 |
| | No. 5 charcoal | 12 | .. | .. |
| | Charcoal dust | 7 | 17 | 12 |
| | | Inch | Inch | Inch |
| Length of case | | 3 | 4 1/4 | 13 |
| Outside diameter | | 1/2 | 11/16 | 2 3/8 |
| Inside diameter | | 5/16 | 7/16 | 1 1/2 |
| Overall length of spindle | | 2 3/4 | 4 | 12 3/4 |
| Length of taper | | 2 1/2 | 3 23/32 | 12 |
| Choke diameter | | 5/32 | 1/4 | 3/4 |

the base of the spindle is, of course, the same as the inside diameter of the case. That of the hemispherical tip of the spindle is half the diameter of the choke, that is, half the diameter of the hole in the clay plug at the base of the rocket. The clay rings and plugs, formed into position by high pressure, actually make grooves in the inner walls of the cases, and these grooves hold them in place against the pressures which arise when the rockets are used. The propelling charge is loaded in several successive small portions by successive pressings with hydraulic presses

[29] Lorrain, *op. cit.*, pp. 236-237.

which handle a gross of the 1-ounce or 3-ounce rockets at a time but only three of the 6-pound size. The presses exert a total pressure of 9 tons on the three spindles when the 6-pound rockets are being loaded.

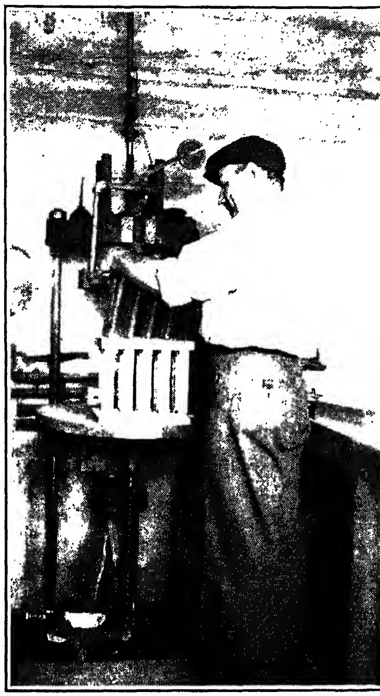


FIGURE 25. Loading Rockets by Means of an Hydraulic Press. (Courtesy National Fireworks Company.)

Rockets of the smaller sizes, for use as toys, are closed at the top with plugs of solid clay and are supplied with conical paper caps. They produce the spectacle only of a trail of sparks streaking skyward. Rockets are generally equipped with sticks to give them balance and direct their flight and are then fired from a trough or frame, but other rockets have recently come on the market which are equipped with vanes and are fired from a level surface while standing in a vertical position.

Large exhibition rockets are equipped with heads which contain stars of various kinds (see below), parachutes, crackers (see grasshoppers), serpents (compare Figure 23), and so on. In these,

the clay plug which stands at the top of the rocket case is perforated, and directly below it there is a *heading* of composition which burns more slowly than the propelling charge. In a typical example this is made from a mixture of saltpeter 24 parts, sulfur 6, fine charcoal 4, willow charcoal dust 1½, and dextrin 2; it is loaded while slightly moist, pressed, and allowed to dry before the head of the rocket is loaded. When the rocket reaches the top of its flight, the heading burns through, and its fire, by means of several strands of black match which have been inserted in the perforation in the clay plug, passes into the head. The head is filled with a mixture, say, of gunpowder, Roman candle composition (see below), and stars. When the fire reaches this mixture, the head blows open with a shower of sparks, and the stars, which have become ignited, fall through the air, producing their own specialized effects.

In another example, the head may contain a charge of gunpowder and a silk or paper parachute carrying a flare or a festoon of lights or colored *twinklers*, the arrangement being such that the powder blows the wooden head from the rocket, ejects the parachute, and sets fire to the display material which it carries. In order that the fire may not touch the parachute, the materials which are to receive the fire (by match from the bursting charge) are packed softly in cotton wool and the remaining space is rammed with bran.

The very beautiful liquid fire effect is produced by equipment which is fully assembled only at the moment when it is to be used. The perforation in the clay plug at the top of the rocket is filled with gunpowder, and this is covered with a layer of waterproof cloth well sealed, separating it from the space in the empty head. When the piece is to be fired, the pyrotechnist, having at hand a can containing sticks of yellow phosphorus preserved under water, removes the wooden head from the rocket, empties the water from the can of phosphorus, and dumps the phosphorus, still wet, into the head case, replaces the wooden head, and fires. The explosion of the gunpowder at the top of the rocket's flight tears through the layer of waterproof cloth, ignites the phosphorus, blows off the wooden head, and throws out the liquid fire. A similar effect, with a yellow light, is obtained with metallic sodium.

## Roman Candles

Roman candles are repeating guns which shoot projectiles of colored fire and send out showers of glowing sparks between the shots. To the pyrotechnists of the seventeenth century they were known as "star pumps" or "pumps with stars."

FIGURE 26. Ramming Roman Candles. (Courtesy National Fireworks Company.)

For the manufacture of Roman candles, gunpowder and stars and a modified black powder mixture which is known as Roman candle composition, or *candle comp*, are necessary. The candle comp is made from:

| | PARTS | |
|---|---|---|
| Saltpeter | 34 | (200 mesh) |
| Sulfur | 7 | (200 mesh) |
| No. 4 Charcoal (hardwood) | 15 | (about 24 mesh) |
| No. 3 Charcoal (hardwood) | 3 | (about 16 mesh) |
| No. 2 Charcoal (hardwood) | 3 | (about 12 mesh) |
| Dextrin | 1 | |

The materials are mixed thoroughly, then moistened slightly and rubbed for intimate mixture through a 10-mesh sieve, dried quickly in shallow trays, and sifted through a 10-mesh sieve.

FIGURE 27. Matching a Battery of 10 Ball Roman Candles. (Courtesy National Fireworks Company and the *Boston Globe.*)

Candle comp burns more slowly than black powder and gives luminous sparks. The case is a long, narrow, strong tube of paper plugged at the bottom with clay. Next to the clay is a small quantity of gunpowder (4F); on top of this is a star; and on top of this a layer of candle comp. The star is of such size that it does not fit the tube tightly. It rests upon the gunpowder, and

the space between the star and the wall of the tube is partly filled with candle comp. When the three materials have been introduced, they are rammed tightly into place. Then gunpowder, a star, and candle comp again are loaded into the tube and rammed down, and so on until the tube is charged. Damp candle comp, with a piece of black match leading to it and into it, is loaded at the top, pressed tightly into place, and allowed to dry. When a Roman candle is lighted, the candle comp begins to burn and to throw out a fountain of sparks. The fire soon reaches the star, ignites it, and flashes along the side of the star to light the gunpowder which blows the burning star, like a projectile, out of the tube.

### Stars

Stars are pellets of combustible material. Those which contain neither aluminum nor magnesium nor Paris green have nothing in their appearance to suggest even remotely the magic which is in them. They are, however, the principal cause of the beauty of aerial pyrotechnic displays.

The components of star composition are mixed intimately and dampened uniformly with some solution which contains a binder, perhaps with gum-arabic water, perhaps with water alone if the composition contains dextrin, perhaps with alcohol if it contains shellac. Several different methods are used for forming the stars.

To make *cut stars*, the damp mixture is spread out in a shallow pan, pressed down evenly, cut into cubes, say 1/4 to 3/4 inch on the side, allowed to dry, and broken apart. Because of their corners, cut stars take fire very readily and are well suited for use in rockets and small aerial bombshells. Cylindrical stars are preferred for Roman candles.

For the preparation of a small number of stars, a *star pump* is a convenient instrument. This consists of a brass tube with a plunger which slides within it. The plunger has a handle and, on its side, a peg which works within a slot in the side of the tube—in such manner that it may be fixed in position to leave at the open end of the tube a space equal to the size of the star which it is desired to make. This space is then tightly packed with the damp mixture; the plunger is turned so that the peg may move through the longitudinal slot, and the handle is pushed to eject the star.

For large-scale production, a *star plate* or *star mold* assembly is best. This consists of three flat rectangular plates of hard wood or metal, preferably aluminum. One has a perfectly smooth surface. The second, which rests upon this, has many circular holes of the size of the stars which are desired. The damp mixture is dumped upon this plate, rubbed, pressed, and packed into the holes, and the surface of the plate is then wiped clean. The third

FIGURE 28. A Star Plate or Star Board in Use. (Courtesy National Fireworks Company.)

plate is supplied with pegs, corresponding in number and position to the holes of the second plate, the pegs being slightly narrower than the holes and slightly longer than their depth. The second plate is now placed above a tray into which the stars may fall, and the stars are pushed out by putting the pegged plate upon it. In certain conditions it may be possible to dispense with the pegged plate and to push out the stars by means of a roller of soft crêpe rubber.

*Box stars* are less likely to crumble from shock, and are accordingly used in large aerial bombshells. They are also used for festoons and for other aerial tableaux effects. Short pieces of

4-ply manila paper tubing, say $\frac{3}{4}$ inch long and $\frac{1}{2}$ inch in diameter, are taken; pieces of black match long enough to protrude from both ends of the tubes are inserted and held in this position by the fingers while the tubes are pressed full of the damp composition. Box stars require a longer drying than those which are not covered.

White stars, except some of those which contain aluminum, are generally made with potassium nitrate as the oxidizing agent. Various white star compositions are tabulated below. The last three are for white *electric stars.* The last formula, containing perchlorate, was communicated by Allen F. Clark.

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Potassium nitrate | 70 | 28 | 180 | 20 | 42 | 14 | 28 | .. |
| Potassium perchlorate | .. | .. | .. | .. | .. | .. | .. | 30 |
| Barium nitrate | .. | .. | .. | .. | .. | .. | .. | 5 |
| Aluminum | .. | .. | .. | .. | .. | 3 | 5 | 22 |
| Antimony sulfide | 20 | .. | 10 | .. | .. | 3 | 7 | .. |
| Antimony metal | .. | 5 | 40 | .. | .. | .. | .. | .. |
| Zinc dust | .. | .. | .. | .. | 6 | .. | .. | .. |
| Realgar | .. | .. | .. | 6 | 6 | .. | .. | .. |
| Meal powder | .. | .. | .. | .. | 12 | 6 | 3 | .. |
| Sulfur | 20 | 8 | 50 | 6 | 23 | .. | 8 | .. |
| Charcoal dust | .. | .. | 3 | .. | .. | .. | .. | .. |
| Dextrin | 3 | 1 | 6 | 1 | .. | 1 | 1 | .. |
| Shellac | .. | .. | .. | .. | .. | .. | .. | 3 |

Stars which contain aluminum are known as electric stars because of the dazzling brilliancy of their light, which resembles that of an electric arc. Stars which contain chlorate and sulfur or antimony sulfide or arsenic sulfide or picric acid are dangerous to mix, likely to explode if subjected to too sudden shock, and unsafe for use in shells. They are used in rockets and Roman candles. Perchlorate compositions, and chlorate compositions without sulfur, sulfides, and picric acid, will tolerate considerable shock and are used in aerial bombshells.

The following star compositions which contain both chlorate and sulfur are among those recommended by Tessier.[30] Mixtures which contain chlorate and sulfur have a tendency to "sour" with the production of sulfuric acid after they have been wetted,

[30] *Op. cit.,* pp. 338, 343, 344, 345, 347, 349.

and to deteriorate, but the difficulty may be remedied by the addition of an anti-acid, and some of these compositions do in-

FIGURE 29. Aluminum Stars from a Single Rocket.

deed contain carbonates or basic salts which act in that capacity. Tessier recommends that the mixtures be made up while dampened with small quantities of 35 per cent alcohol.

| | Red | Lilac | Lilac Mauve | Violet | Blue | Green |
|---|---|---|---|---|---|---|
| Potassium chlorate | 167 | 17 | 17 | 56 | 24 | 48 |
| Strontium carbonate | 54 | 9 | 9 | .. | .. | .. |
| Strontium sulfate | .. | .. | .. | 16 | .. | .. |
| Barium nitrate | .. | .. | .. | .. | .. | 80 |
| Copper oxychloride | .. | 2 | 4 | .. | .. | .. |
| Basic copper sulfate | .. | .. | .. | 8 | 12 | .. |
| Lead chloride | .. | 1 | 1 | 3 | 2 | 10 |
| Charcoal dust (poplar) | .. | .. | .. | 3 | .. | .. |
| Sulfur | 35 | 7 | 7 | 20 | 8 | 26 |
| Dextrin | 7 | 1 | 1 | 3 | 1 | 3 |
| Shellac | 16 | .. | .. | .. | .. | 2 |
| Lampblack | .. | .. | .. | .. | .. | 2 |

Weingart[31] reports compositions for cut, pumped, or candle stars which contain chlorate but no sulfur or sulfides, as follows:

| | Red | | Blue | Green | Yellow | |
|---|---|---|---|---|---|---|
| Potassium chlorate... | 12 | 48 | 48 | 12 | 32 | 16 |
| Strontium nitrate.... | 12 | | | | | |
| Strontium carbonate. | | | | | | |
| Barium nitrate...... | | | 16 | 12 | 12 | |
| Paris green......... | | | 18 | .. | | |
| Calomel............ | | | | 1 | | |
| Sodium oxalate...... | | | | | | |
| Fine charcoal....... | | | | | | |
| Dextrin............ | | | 3 | | | |
| Shellac............ | | | 10 | | | |

For the following perchlorate star formulas the author is indebted to Allen F. Clark.

| | Rose | Amber | Green | | Violet | |
|---|---|---|---|---|---|---|
| Potassium perchlorate.......... | 12 | 10 | .. | 44 | 12 | 41 |
| Potassium nitrate.............. | 6 | .. | .. | .. | .. | .. |
| Barium perchlorate............ | .. | .. | 32 | 90 | .. | .. |
| Calcium carbonate............. | .. | .. | .. | .. | .. | 12 |
| Strontium oxalate............. | 1 | .. | .. | .. | 9 | 3 |
| Copper oxalate................ | .. | .. | .. | .. | 5 | .. |
| Sodium oxalate................ | .. | 4 | .. | .. | .. | .. |
| Calomel....................... | .. | .. | .. | .. | .. | 3 |
| Sulfur........................ | .. | .. | .. | .. | .. | 14 |
| Lampblack.................... | 1 | .. | .. | .. | .. | .. |
| Dextrin...................... | 1 | .. | .. | 6 | .. | .. |
| Shellac...................... | .. | 2 | 3 | 15 | 3 | .. |

Illustrative of electric star compositions are the following; those which contain potassium chlorate are reported by Faber,[32] the others, containing perchlorate, were communicated by Allen

[31] *Op. cit.*, p. 114.
[32] *Op. cit.*, Vol. 1, p. 188.

| | Red | | Gold | Green | | | Blue | |
|---|---|---|---|---|---|---|---|---|
| Potassium perchlorate | .. | 12 | .. | .. | .. | 6 | .. | 14 |
| Potassium chlorate | 24 | .. | 6 | 8 | .. | .. | 32 | .. |
| Barium perchlorate | .. | .. | .. | .. | 12 | 12 | .. | .. |
| Barium chlorate | .. | .. | 4 | 16 | .. | .. | .. | .. |
| Barium nitrate | .. | .. | .. | 16 | .. | .. | .. | .. |
| Strontium chlorate | .. | 3 | .. | .. | .. | .. | .. | .. |
| Strontium carbonate | 4 | .. | .. | .. | .. | .. | .. | .. |
| Aluminum | 8 | 3 | 4 | 12 | 5 | 8 | 8 | 6 |
| Sodium oxalate | .. | .. | 2 | .. | .. | .. | .. | .. |
| Calcium carbonate | .. | .. | .. | .. | .. | .. | .. | 1 |
| Magnesium carbonate | .. | .. | 1 | .. | .. | .. | .. | .. |
| Paris green | .. | .. | .. | .. | .. | .. | 16 | 10 |
| Calomel | .. | .. | .. | .. | .. | .. | .. | 2 |
| Fine charcoal | 1 | .. | .. | 3 | .. | .. | .. | .. |
| Dextrin | 2 | 1 | .. | 2 | .. | 1 | 2 | 1 |
| Red gum | .. | .. | .. | 4 | .. | .. | .. | .. |
| Shellac | 2 | 1 | 2 | .. | 1 | 2 | 1 | 2 |

F. Clark. The last-named authority has also supplied two formulas for magnesium stars. The compositions are mixed while

| | Amber | Green |
|---|---|---|
| Potassium perchlorate | 4 | .. |
| Barium perchlorate | .. | 12 |
| Magnesium | 1 | 2 |
| Sodium oxalate | 2 | .. |
| Lycopodium powder | .. | 1 |
| Shellac | 1 | 2 |

dampened with alcohol which insures that the particles of magnesium are covered with a protective layer of shellac.

*Lampblack stars* burn with a rather dull soft light. Discharged in large number from a rocket or aerial shell, they produce the beautiful willow-tree effect. They are made, according to Allen F. Clark, by incorporating 3 pounds of lampblack, 4 pounds of meal powder, and ½ pound of finely powdered antimony sulfide with 2 ounces of shellac dissolved in alcohol.

Stars compounded out of what is essentially a modified black

powder mixture, given a yellowish or whitish color by the addition of appropriate materials, and used in rockets and shells in the same manner as lampblack stars, produce *gold* and *silver showers*, or, if the stars are larger and fewer in number, *gold* and *silver streamers*. The following formulas are typical.

| | Gold | Silver |
|---|---|---|
| Potassium nitrate | 16 | 10 |
| Charcoal | 1 | 2 |
| Sulfur | 4 | 3 |
| Realgar | .. | 3 |
| Sodium oxalate | 8 | .. |
| Red gum | 1 | 1 |

*Twinklers* are stars which, when they fall through the air, burn brightly and dully by turns. A shower of twinklers produces an extraordinary effect. Weingart in a recent letter has kindly sent the following formula for yellow twinklers:

| | |
|---|---|
| Meal powder | 24 |
| Sodium oxalate | 4 |
| Antimony sulfide | 3 |
| Powdered aluminum | 3 |
| Dextrin | 1 |

The materials are mixed intimately while dampened with water, and the mixture is pumped into stars about ¾ inch in diameter and ⅞ inch long. The stars are dried promptly. They function only when falling through the air. If lighted on the ground they merely smolder, but when fired from rockets or shells are most effective.

*Spreader stars* contain nearly two-thirds of their weight of powdered zinc. The remaining one-third consists of material necessary to maintain an active combustion. When they are ignited, these stars burn brightly and throw off masses of burning zinc (greenish white flame) often to a distance of several feet. Weingart[33] gives the two following formulas for spreader stars, the first for "electric spreader stars," the second for "granite stars," so called because of their appearance.

[33] *Op. cit.*, p. 118.

| | | |
|---|---|---|
| Zinc dust | 72 | 80 |
| Potassium nitrate | .. | 28 |
| Potassium chlorate | 15 | .. |
| Potassium dichromate | 12 | .. |
| Granulated charcoal | 12 | .. |
| Fine charcoal | .. | 14 |
| Sulfur | .. | 5 |
| Dextrin | 2 | 2 |

The first of these formulas is the more difficult to mix and the more expensive. All its components except the charcoal are first

FIGURE 30. Spreader Stars from a Battery of Rockets.

mixed and dampened; the granulated charcoal, which must be free from dust, is then mixed in, and the stars are formed with a pump. They throw off two kinds of fire when they burn, masses of brightly burning zinc and particles of glowing charcoal. Weingart recommends that the second formula be made into cut stars ⅜ inch on the side. Spreader stars because of the zinc which they contain are much heavier than other stars. Rockets and aerial bombs cannot carry as many of them.

## Gerbs

Gerbs produce jets of ornamental and brilliant fire and are used in set pieces. They are rammed or pressed like rockets, on a short nipple instead of a long spindle, and have only a slight depression within the choke, not a long central cavity. They are choked to about one-third the diameter of the tube. The simplest gerbs contain only a modified black powder mixture, say meal powder 4 parts, saltpeter 2, sulfur 1, and charcoal dust 1 or mixed charcoal 2; and are used occasionally for contrast in elaborate set pieces. Similar composition is used for the starting fire of steel gerbs which are more difficult to ignite. If antimony sulfide is used in place of charcoal, as in the mixtures:

| | | |
|---|---|---|
| Meal powder | 2 | 3 |
| Saltpeter | 8 | 8 |
| Sulfur | 3 | 4 |
| Antimony sulfide | 1 | 2 |

the gerbs yield compact whitish flames and are used in star and floral designs. Gold gerbs appropriately arranged produce the sunburst effect. Colored gerbs are made by adding small cut stars. In loading the tube, a scoopful of composition is introduced and rammed down, then a few stars, then more composition which is rammed down, and so on. Care must be exercised that no stars containing chlorate are used with compositions which contain sulfur, for an explosion might occur when the charge is rammed. The following compositions are typical. The steel filings

| | Steel | Colored Steel | Gold | Colored Gold |
|---|---|---|---|---|
| Meal powder | | 8 | 40 | 40 |
| Potassium nitrate | | 7 | .. | |
| Sulfur | | .. | .. | |
| Fine charcoal | | 2 | .. | |
| Steel filings | | 5 | .. | |
| Stars | | 5 | .. | |
| Sodium oxalate | | .. | 6 | |
| Antimony sulfide | | .. | 8 | |
| Aluminum | | .. | 4 | |
| Dextrin | | .. | .. | |

must be protected from rusting by previous treatment with paraffin or linseed oil.

*Prismatic fountains, floral bouquets,* etc., are essentially colored gerbs. Flower pots are supplied with wooden handles and generally contain a modified black powder composition with lampblack and sometimes with a small amount of granulated black powder. In the charging of fountains and gerbs, a small charge of gunpowder is often introduced first, next to the clay plug which closes the bottom of the tube and before the first scoopful of composition which is rammed or pressed. This makes them finish with a report or *bounce.*

### Fountains

Fountains are designed to stand upon the ground, either upon a flat base or upon a pointed wooden stick. They are choked slightly more than gerbs, and have heavier, stronger cases to withstand the greater pressures which eject the fire to greater distances.

The "Giant Steel Fountain" of Allen F. Clark is charged with a mixture of saltpeter 5 parts (200 mesh), cast-iron turnings 1 part (8 to 40 mesh), and red gum 1 part (180 to 200 mesh). For loading, the mixture is dampened with 50 per cent alcohol. The case is a strong paper tube, 20 inches long, 4 inches in external diameter, with walls 1 inch thick, made from Bird's hardware paper. It is rolled on a machine lathe, the paper being passed first through a heavy solution of dextrin and the excess of the gum scraped off. The bottom of the case is closed with a 3-inch plug of clay. The composition will stand tremendous pressures without exploding, and it is loaded very solidly in order that it may stay in place when the piece is burned. The charge is rammed in with a wooden rammer actuated by short blows, as heavy as the case will stand, from a 15-pound sledge. The top is closed with a 3-inch clay plug. A ⅞-inch hole is then bored with an auger in the center of the top, and the hole is continued into the charge to a total depth of 10 inches. The composition is difficult to light, but the ignition is accomplished by a bundle of six strands of black match inserted to the full depth of the cavity and tied into place. This artifice produces a column of scintillating fire, 100 feet or more in height, of the general shape of a red cedar tree. It develops considerable sound, and ends sud-

denly with a terrifying roar at the moment of its maximum splendor. If loaded at the hydraulic press with a tapered spindle (as is necessary), it finishes its burning with a fountain which grows smaller and smaller and finally fades out entirely.

### Wheels

Driving tubes or *drivers*, attached to the periphery of a wheel or to the sides of a square or hexagon of wood which is pivoted

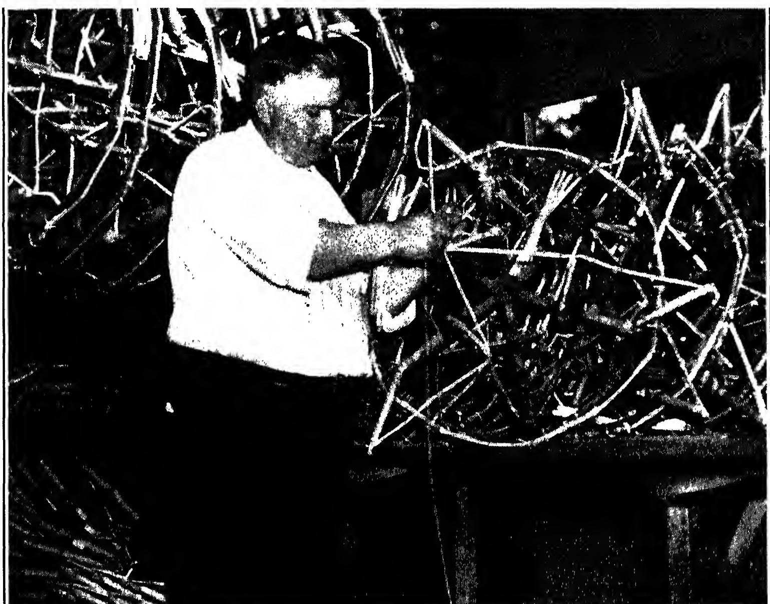


FIGURE 31. Matching Display Wheels. (Courtesy National Fireworks Company and the *Boston Globe*.)

at its center, by shooting out jets of fire, cause the device to rotate and to produce various ornamental effects according to the compositions with which they are loaded. When the fire reaches the bottom of one driver, it is carried by quickmatch to the top of the next. Drivers are loaded in the same manner as gerbs, the compositions being varied slightly according to the size as is done with rockets. A gross of the 1-ounce and 2-ounce sizes in present American practice is loaded at one time by the hydraulic press. Typical wheel turning compositions (Allen F. Clark) for

use in 1-ounce and 2-ounce drivers are reported below, the first for a *charcoal spark effect,* the second for an *iron and steel effect.* The speed of the mixtures may be increased by increasing the proportion of gunpowder.

| | | |
|---|---|---|
| Saltpeter (210 mesh) | 10 | 46 |
| Sulfur (200 mesh) | 2 | 19 |
| Meal powder | 6 | .. |
| Charcoal dust | .. | 16 |
| Charcoal (80 mesh) | 1 | .. |
| 6F gunpowder | 6 | .. |
| 7F gunpowder | .. | 24 |
| Cast-iron turnings (16 mesh) | .. | 30 |
| Dextrin | .. | 8 |

Wheels, gerbs, and colored fires are the parts out of which such display pieces as the "Corona Cluster," "Sparkling Caprice," "Flying Dutchman," "Morning Glory," "Cuban Dragon," "Blazing Sun," and innumerable others are constructed.

## Saxons

Saxons are strong paper tubes, plugged with clay at their middles and at both ends, and filled between the plugs with composition similar to that used in drivers. A lateral hole is bored through the middle of the tube and through the central clay plug, and it is around a nail, passed through this hole and driven into a convenient support, that the artifice rotates. Other holes, at right angles to this one, are bored from opposite sides near the ends of the tube, just under the end plugs, through one wall of the tube and into the composition but not through it. A piece of black match in one of these holes ignites the composition. The hot gases, sparks, etc., rushing from the hole cause the device to turn upon its pivot. When the fire reaches the bottom of the charge, it lights a piece of quickmatch, previously connected through a hole at that point and glued to the outside of the case, which carries the fire to the other half of the saxon.

Saxons are generally matched as described, the two halves burning consecutively and rotating it in the same direction. Sometimes they burn simultaneously, and sometimes one half turns it in one direction and the other afterwards "causes the rapid spinning to reverse amid a mad burst of sparks." This effect "is very pleasing and is considered one of the best to be obtained for so small an expenditure."

### Pinwheels

To make pinwheels, manila or kraft paper tubes or *pipes*, about 12 inches long and 3/16 inch in diameter, are needed. One end is closed by twisting or folding over. The tubes are filled with composition, the other ends are closed in the same way, and the tubes are wrapped in a moist towel and set aside until they are thoroughly flabby. In this condition they are passed between rollers and flattened to the desired extent. Each tube is then wound in an even spiral around the edge of a cardboard disc which has a hole in its center for the pin, and the whole is placed in a frame which prevents it from uncoiling. Four drops of glue, at the four quarters of the circle, are then brushed on, across the pipes and onto the center disc, and the device is allowed to dry.

Weingart[34] recommends for pinwheels the compositions which are indicated below. The first of these produces both steel and

| | | | | |
|---|---|---|---|---|
| Meal powder | .. | 10 | 8 | 2 |
| Gunpowder (fine) | 8 | 5 | 8 | .. |
| Aluminum | .. | .. | 3 | .. |
| Saltpeter | 14 | 4 | 16 | 1 |
| Steel filings | 6 | 6 | .. | .. |
| Sulfur | 4 | 1 | 3 | 1 |
| Charcoal | 3 | 1 | 8 | .. |

charcoal effects, the second steel with much less of the charcoal, the third aluminum and charcoal, and the fourth a circle merely of lilac-colored fire.

Tessier thought highly of pinwheels (*pastilles*). They were, he says,[35]

> formerly among the artifices which were called *table fireworks*, the use of which has wholly fallen away since the immense apartments have disappeared which alone provided places where these little pyrotechnic pieces might be burned without too much inconvenience.
>
> The manner of use of these pastilles calls only for small calibers; also their small dimensions make it possible to turn them out at a low price, and the fireworks makers have always continued to make them the object of current manufacture. But what they have neglected, they still neglect: and that is, to seek to bring them to perfection. Those that

[34] *Op. cit.*, p. 98.
[35] *Op. cit.*, p. 393.

they confine themselves to making serve only for the amusement of children.

However, pastilles may become charming pieces of fireworks, fit to refresh all eyes. They can be made to produce

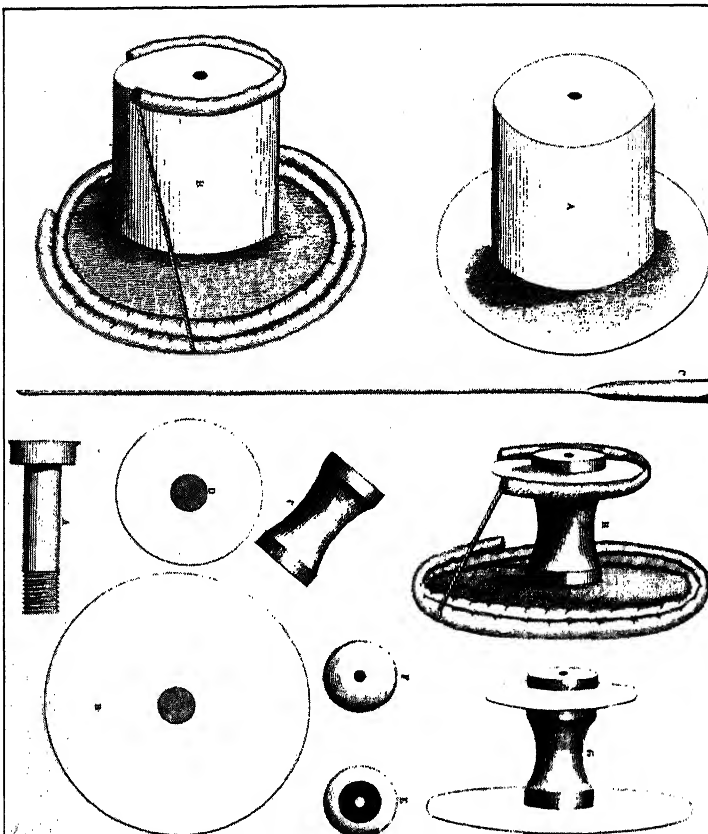


FIGURE 32. Pinwheels, Tessier, 1883. Wheels which show an inner circle of colored fire. Plate 1 (above) pictures pinwheels which are intended to be sold as completely consumable. The instrument represented at the bottom of the plate is the ramrod for tamping the charges in the pipes. Plate 2 (below) represents pinwheels which are intended to be exhibited by the pyrotechnist himself: the wooden parts are to be recovered, and used again.

truly marvellous effects, considering the conditions imposed by their size, effects all the more remarkable in as much as, by the very reason of these same conditions, they have no

> need of a vast theater in which to be fired. The least little garden suffices for them. They burn under the very eye of the spectator, who loses nothing of their splendor, whereas, in general, large pieces of fireworks can be enjoyed only at a distance from the place of firing. Finally, they have over these last the advantage of their low price and the advantage that they can be transported without embarrassment and set in place at the moment of being fired.

Tessier describes ordinary pastilles, diamond pastilles, and pastilles with colored fires. The shorter and more central tubes (Figure 32), wound part way around discs 40 mm. in diameter, hold the colored fire compositions. The longer tubes, forming the larger circles around discs 72 mm. in diameter, are the turning tubes. The latter, it will be seen, are so arranged that they burn for a time before the fire reaches the colored compositions. "The charging of the tubes is commenced, up to a height of about 17 cms., with the four compositions, Nos. 142, 126, 128, and 129, in the order named. The rest of the tube is charged entirely with composition No. 149, or with No. 152, both of which produce scintillating aureoles."[36] The charges are tamped tightly in the tubes by means of a long, thin ramrod and mallet. The compositions in question, designated by Tessier's own numbers, are indicated below.

| | 142 | 126 | 128 | 129 | 149 | 152 |
|---|---|---|---|---|---|---|
| Meal powder | 16 | 16 | 16 | 32 | .. | .. |
| Potassium nitrate | 1 | 1 | 1 | 4 | .. | .. |
| Oak charcoal | 1 | .. | .. | .. | .. | .. |
| Litharge | .. | 2 | .. | .. | .. | .. |
| Powdered mica | .. | .. | 2 | .. | .. | .. |
| Antimony sulfide | .. | .. | .. | 5 | .. | .. |
| Plumbic powder No. 1 | .. | .. | .. | .. | 17 | 17 |
| Cast-iron filings | .. | .. | .. | .. | 3 | .. |
| Steel wool | .. | .. | .. | .. | .. | 3 |

No. 142 is a composition for ordinary pastilles. Tessier says that it produces "numerous sparks forming a feeble aureole. As this composition is not lively, and as it is not able to make the

[36] *Ibid.*, p. 419.

pastilles turn conveniently, care is taken not to load more of it than a length of 15 mm. in the tube."[37]

Nos. 126, 128, and 129 are also for ordinary pastilles. No. 126 "has not much force; it is incapable alone of making a pastille turn with the necessary rapidity. Hence care is taken in charging it to introduce only a small quantity into the tube." It burns with a white flame "forming a crown, more or less lacy-edged, from which rays and sparks are thrown out."[38]

The two compositions, Nos. 142 and 126, evidently burn while the pastille is turning from the initial twirl given it by the hand. When the fire reaches the next composition, No. 128, the pastille accelerates by its own power. This gives "reddish rays, very straight and very numerous," and No. 129 gives "a white flame around the disc, and numerous and persistent sparks which fall down forming a sort of cascade on each side of the pastille."[39]

Neither No. 128 nor 129 is bright enough to make much of a show if the colored fire is also burning. When they burn to an end, the fire is communicated to the colored composition; at the same time the bright diamond composition, either No. 149 or 152, commences to burn. No. 149 produces "a splendid aureole of silver-white flowers. These flowers are less developed than those produced by steel wool and make a different effect from the latter."[40] No. 152 produces a "splendid effect—no inflamed disc, no reddish sparks—numerous jasmine flowers of all dimensions forming a vast aureole of a striking white."[41]

Plumbic powder No. 1 is made from lead nitrate 12 parts, potassium nitrate 2 parts, and black alder charcoal 3 parts.[42] The materials are powdered and mixed, and then rolled in a wooden ball-mill with balls of hard lead (Pb 5, Sb 1) or brass or bronze.

Tessier[43] gives credit to the earlier French pyrotechnist, Chertier, for the introduction into pyrotechny of lead nitrate (which had been used before his time only for the preparation of slow-

[37] *Ibid.*, p. 408.
[38] *Ibid.*, p. 403.
[39] *Ibid.*, p. 404.
[40] *Ibid.*, p. 411.
[41] *Ibid.*, p. 412.
[42] *Ibid.*, p. 281.
[43] *Op. cit.*, p. 118.

match or fire wick), for the invention[44] of plumbic powder by which a silver shower (*pluie d'argent*) is produced, and for originating[45] the idea of the diamond pastille with colored fires which Chertier called the *dahlia pastille* but for the making of which he did not give precise directions.

## Mines

Mines are paper mortars—commonly strong paper tubes each standing vertically on a wooden base into which it is countersunk and glued—arranged to throw into the air a display of stars, serpents, etc. They are often equipped with fountains, Roman candles, etc., which make a display on the ground before the final explosion occurs.

A *serpent mine* (*pot à feu*) is represented in Figure 24. This starts with a steel fountain. When the fire has reached the bottom of the fountain, it is carried by quickmatch to a charge of gunpowder in the paper bag, *a*. Immediately above the paper bag are the serpents. These are small paper tubes, rammed with a mixture of meal powder, gunpowder, saltpeter, sulfur, and mixed charcoal, crimped or plugged with clay at one end, supplied with match (as in the diagram) or merely left open-ended at the other. The lower, matched or open, ends of the serpents take fire from the burning of the gunpowder, which also blows them into the air where they dart and squirm about like little tailless rockets leaving a trail of sparks. In Audot's diagram, directly below the fountain and above the closed ends of the serpents, is a mass of wadding. This tends to offer a slight resistance to the force of the gunpowder, with the result that the serpents receive the fire more surely and are shot farther into the air before they begin to go their several ways.

Saucissons are constructed in the same way as serpents, but are larger, and have, next to the closed end, a small charge of gunpowder which makes them end with a bang. They are used in mines and in rockets.

Mines which discharge serpents, stars, English crackers, etc., are often made by loading these materials into the same paper bags which contain the blowing charges of granulated gunpowder. About two level teaspoonfuls of blowing powder is used

[44] *Ibid.*, p. 281.
[45] *Ibid.*, p. 414.

per ounce of stars. For making the bags, a board is taken which has had holes bored into it slightly smaller than the internal diameter of the mine case and of a depth suited to the caliber of the mine. A disc of tissue paper is placed over a hole and then punched down into it by a wooden punch or rod with slightly rounded edges which fits rather loosely in the hole. This makes a paper cup into which one end of the fuse is inserted, and around it the stars and blowing charge. The edges of the paper cup are then gathered together and tied with string or wire.

Mines are often made up with a single Roman candle, lacking the plug of clay at the bottom, mounted in the center of the mine case. The fuse leading from the charge in the paper bag is thrust into the bottom of the Roman candle. A mine with a large and short case, carrying a charge of tailed stars, serpents, and English crackers, and having one Roman candle in its center and four others, matched to burn simultaneously, attached to the outside of the case, is known as a *devil among the tailors*.

### Comets and Meteors

These are virtually mines which shoot a single large star. A pumped star 1½ inches in diameter is fired, for example, from a tube or mortar 10 inches long and 1¾ inches in internal diameter. A piece of quickmatch (wrapped black match) about 6 inches longer than the mortar is taken; an inch of black match is made bare at one end, bent at right angles, and laid against the base of the star; and the star, with the quickmatch lying along its side, is then enclosed in the middle of a paper cylinder by wrapping a strip, say 4 inches wide, of pasted tissue paper around it. A half teaspoonful of granulated black powder is put into the cup thus formed on the (bottom) side of the star where the black match has been exposed, and the edges of the paper cylinder are brought together over it and tied. The other (upper) end of the paper cylinder is similarly tied around the quickmatch. In using this piece, and in using all others which are lighted by quickmatch, care must be taken that a few inches of the quickmatch have been opened and the black match exposed, before the fire is set to it; otherwise it will be impossible to get away quickly enough. This, of course, is already done in pieces which are offered for public sale.

Comets burn with a charcoal or lampblack effect, meteors with

an electric one. The two comet star compositions given below are due to Weingart;[46] that of the green meteor to Allen F. Clark.

| | Comets | | Green Meteor |
|---|---|---|---|
| Potassium nitrate | 6 | .. | .. |
| Barium perchlorate | .. | .. | 4 |
| Barium nitrate | .. | .. | 2 |
| Meal powder | 6 | 3 | .. |
| Sulfur | 1 | .. | .. |
| Fine charcoal | 3 | 1 | .. |
| Antimony sulfide | 3 | 1 | .. |
| Lampblack | .. | 2 | .. |
| Aluminum | .. | .. | 1 |
| Dextrin | .. | .. | 1 |

Some manufacturers apply the name of meteors to artifices which are essentially large Roman candles, mounted on wooden bases and shooting four, six, eight, and ten stars 1½ inches in diameter. They are loaded in the same way as Roman candles except that a special device is used to insure the certain ignition of the stars. Two pieces of black match at right angles to each other are placed under the bottom of the star; the four ends are turned up along the sides of the star and are cut off even with the top of it. The match being held in this position, the star is inserted into the top of the case and pushed down with a rammer onto the propelling charge of gunpowder which has already been introduced. Then coarse candle comp is put in, then gunpowder, then another star in the same manner, and so on. The black match at the side of the star keeps a space open between the star and the walls of the tube, which space is only partly or loosely filled with candle comp. The black match acts as a quickmatch, insuring the early ignition of the propelling charge as well as the sure ignition of the star. Electric stars, spreader stars, and *splitters* are used in meteors. Splitter stars are made from the same composition as snowball sparklers (see below); the composition for stars, however, is moistened with much less water than for sparklers. They split into bright fragments while shooting upward and burst at the top to produce a palm-tree effect.

[46] *Op. cit.*, p. 121

### Bombshells

Bombshells are shot from mortars by means of a charge of black powder and burst high in the air with the production of reports, flashes, showers, and other spectacular effects. The smaller ones are shot from paper mortars; the larger, most commonly from mortars of iron. In the past they have often been made in a spherical shape, wood or paper or metal hemispheres pasted heavily over with paper, but now in this country they are made almost exclusively in the form of cylinders. For the same caliber, cylindrical bombshells will hold more stars or other display material than spherical ones, and it is much easier to contrive them in a manner to procure multiple bursts. The materials of construction are paper, paste, and string. The shells are supplied with *Roman fuses* timed to cause them to burst at the top of their flight. The success and safety of bombshells depend upon carefully constructed fuses.

Roman fuses are made by pounding the fuse powder as firmly as is possible into hard, strong, tightly rolled paper tubes. These are commonly made from Bird's hardware paper, pasted all over before it is rolled, and are dried carefully and thoroughly before they are loaded with ramrod and mallet. "When a number of these cases are rolled," says Weingart,[47] "they must be dried in the shade until they are as hard as wood and rattle when struck together." He recommends the first of the following-listed compositions, the Vergnauds the others:[48]

| | | | |
|---|---|---|---|
| Potassium nitrate...... | 2 | 4 | 2 |
| Sulfur................. | 1 | 2 | 1 |
| Meal powder.......... | 4 | 6 | 3 |
| Antimony sulfide...... | .. | 1 | .. |

The length of the column of composition determines the duration of the burning. The composition in the fuse must be as hard and as firmly packed as possible; otherwise it will blow through into the shell when in use and will cause a premature explosion. Some manufacturers load the tubes and cut them afterwards with a fine-tooth hack saw. Others prefer to cut them to the desired lengths with a sharp knife while they are prevented from collapsing by a brass rod through them, and afterwards to load

[47] *Ibid.*, p. 130.

[48] A. D. and P. Vergnaud, "Nouveau manuel complet de l'artificier. Pyrotechnie civile." (Ed., G. Petit) (Manuels Roret), Paris, 1906.

the short pieces separately. Different size tubes are often used for the fuses of different size shells; those for a 4-inch shell (that is, for a shell to be shot from a 4-inch mortar) are commonly made from tubes 5/16 inch in internal diameter and ⅝

FIGURE 33. Bombshells for 4- and 6-inch Mortars. (Courtesy National Fireworks Company and the *Boston Globe*.)

inch in external diameter. Fuses are generally attached to the front end of the bombshell. The forward-pointing end of the tube, which is outside the shell and receives the fire, is filled flush with the composition. The other backward-pointing end, inside the shell, is empty of composition for ¾ inch of its length; a

bundle of stiff 2-inch pieces of black match is inserted into this space and is held in position by a rolled wrapper of paper, glued to the fuse case and tied with a string near the ends of the match, in order that it may not be dislodged by the shock of setback. The match serves to bring the fire more satisfactorily to the bursting charge within the shell.

The preparation of the bombshell is hand work which requires much skill and deserves a fairly full description. We describe the construction of a 4-inch shell to produce a single burst of stars. A strip of bogus or news board paper is cut to the desired length and is rolled tightly on a form without paste. When it is nearly all rolled, a strip of medium-weight kraft paper, 4 inches wider than the other strip, is rolled in and is rolled around the tube several times and is pasted to hold it in position. Three circular discs of pasteboard of the same diameter as the bogus tube ($3\frac{1}{2}$ inches) are taken, and a $\frac{5}{8}$-inch hole is punched in the center of two of them. The fuse is inserted through the hole in one of them and glued heavily on the inside. When this is thoroughly dry, the disc is glued to one end of the bogus tube, the matched end of the fuse being outside; the outer wrapper of kraft paper is folded over carefully onto the disc, glued, and rubbed down smoothly; and the second perforated disc is placed on top of it.

The shell case is now turned over, there being a hole in the bench to receive the fuse, and it is filled with as many stars ($\frac{1}{2}$-inch diameter, $\frac{1}{2}$ inch long) as it will contain. A mixture of 2F gunpowder and candle comp is then added, shaken in, and settled among the stars until the case is absolutely full. A disc of pasteboard is placed over the stars and powder, pressed down against the end of the bogus body and glued, and the outer kraft paper wrapper is folded and glued over the end.

At this point the shell is allowed to dry thoroughly before it is wound with strong jute twine. It is first wound lengthwise; the twine is wrapped as tightly as possible and as firmly against the fuse as may be; each time that it passes the fuse the plane of the winding is advanced by about 10° until 36 turns have been laid on, and then 36 turns are wound around the sides of the cylinder at right angles to the first winding. The shell is now ready to be "pasted in." For this purpose, 50-pound kraft paper is cut into strips of the desired dimensions, the length of the strips being across the grain of the paper. A strip of this paper

is folded, rubbed, and twisted in paste until it is thoroughly impregnated. It is then laid out on the bench and the shell is rolled up in it. The cylinder is now stood upright, the fuse end at the top, and the portion of the wet pasted kraft paper wrapper which extends above the body of the shell is torn into strips about ¾ inch wide; these, one by one, are rubbed down carefully and smoothly, one overlapping the other, upon the end of the shell case. They extend up the fuse tube for about ½ inch and are pressed down firmly against it. The shell is now turned over, the fused end resting against a tapered hole in the bench, and a corresponding operation is performed upon the other end. The body of the shell is now about ¼ inch thick on the sides of the cylinder, about ⅜ inch thick at the top end, and about ½ inch at the base end. It is dried outdoors in the sun and breeze, or in a well-ventilated dry-house at 100°F., and, when thoroughly dry, is ready to be supplied with the propelling or *blowing charge*.

A piece of *piped match* (black match in a paper tube) is laid along the side of the bombshell; both are rolled up without paste in 4 thicknesses of 30-pound kraft paper wide enough to extend about 4 inches beyond the ends of the cylinder, and the outer wrapper is tied lightly in place by two strings encircling the cylinder near the ends of the shell case. The cylinder is turned bottom end up. About 3 inches of the paper pipe of the quickmatch is removed to expose the black match, a second piece of black match is inserted into the end of the paper pipe, and the pipe is tied with string to hold the match in place. The propelling charge of 2F gunpowder is next introduced; the two inner layers of the outer kraft paper wrapper are folded down upon it and pressed firmly, then the two outer layers are pleated to the center of the cylinder, tied, and trimmed close to the string. The cylinder is then turned to bring the fuse end uppermost. The end of the fuse is scraped clean if it has been touched with paste. Two pieces of black match are crossed over the end of the fuse, bent down along the sides of the fuse tube, and tied in this position with string. The piped match which leads to the blowing charge is now laid down upon the end of the cylinder, up to the bottom of the fuse tube, then bent up along the side of the fuse tube, then bent across its end and down the other side, and then bent

back upon itself, and tied in this position. Before it is tied, a small hole is made in the match pipe at the point where it passes the end of the Roman fuse, and a piece of flat black match is inserted. The two inner layers of the kraft paper wrapper are now pleated around the base of the fuse and tied close to the shell. The two outer layers are pleated and tied above the top of the fuse, a 3-foot length of piped match extending from the upper end of the package. A few inches of black match is now bared at the end and an extra piece of black match is inserted and tied in place by a string about 1 inch back from the end of the pipe. The black match, for safety's sake, is then covered with a piece of lance tube, closed at the end, which is to be removed after the shell has been placed in the mortar and is ready for firing.

## Maroons

Bombs which explode with a loud report, whether they are intended for use on the ground or in the air, are known as maroons. They are called *marrons* in French, a name which also means large chestnuts in that language—and chestnuts sometimes explode while being roasted.

Maroons are used for military purposes to disconcert the enemy by imitating the sounds of gunfire and shell bursts, and have at times been part of the standard equipment of various armies. A cubical pasteboard box filled with gunpowder is wound in three directions with heavy twine, the successive turns being laid close to one another; an end of miner's fuse is inserted through a hole made by an awl, and the container, already very strong, is made still stronger by dipping it into liquid glue and allowing to dry.

For sharper reports, more closely resembling those of a high-explosive shell, fulminating compositions containing chlorate are used. With these, the necessity for a strong container is not so great; the winding may be done with lighter twine, and the successive turns of twine need not make the closest possible contact. Faber reports two compositions, as follows:

| | | |
|---|---|---|
| Potassium chlorate | 4 | 1 |
| Sulfur | 1 | .. |
| Soft wood charcoal | 1 | .. |
| Antimony sulfide | .. | 1 |

"It is to be noted," he says,[49] "that, while the first formula affords a composition of great strength, the second is still more violent. It is also of such susceptibility that extraordinary care is required in the handling of it, or a premature explosion may result."

Chlorate compositions are not safe for use in maroons. Black powder is not noisy enough. Allen F. Clark has communicated the following perchlorate formulas for reports for maroons. For

| | | | |
|---|---|---|---|
| Potassium perchlorate | 12 | 6 | 32 |
| Sulfur | 8 | 2 | .. |
| Antimony sulfide | .. | 3 | .. |
| Sawdust | 1 | .. | .. |
| Rosin | .. | .. | 3 |
| Fine charcoal | .. | .. | 3 |

a *flash report* he uses a mixture of 3 parts of potassium permanganate and 2 of aluminum.

## Toy Caps

Toy caps are commonly made from red phosphorus and potassium chlorate, a combination which is the most sensitive, dangerous, and unpredictable of the many with which the pyrotechnist has to deal. Their preparation ought under no conditions to be attempted by an amateur. Powdered potassium chlorate 20 parts is made into a slurry with gum water. It is absolutely essential that the chlorate should be wetted thoroughly before the red phosphorus is mixed with it. Red phosphorus, 8 parts, is mixed with powdered sulfur 1 part and precipitated calcium carbonate 1 part, and the mixture is made into a slurry separately with gum water, and this is stirred into the other until thoroughly mixed. The porridgelike mass is then spotted on paper, and a piece of pasted tissue paper is placed over the spotted surface in a manner to avoid the enclosure of any air bubbles between the two. This is important, for, unless the tissue paper covers the spots snugly, the composition is likely to crumble, to fall out, and to create new dangers. (A strip of caps, for example, may explode between the fingers of a boy who is tearing it.) The moist sheets of caps are piled up between moist blankets in a press, or with a board and weights on top of the pile, and are pressed for an hour or so. They are then cut into strips

[49] *Op. cit.*, Vol. 1, p. 166.

of caps which are dried, packaged, and sold for use in toy repeating pistols. Or they are cut in squares, one cap each, which are not dried but are used while still moist for making Japanese torpedoes (see below). The calcium carbonate in this mixture is an anti-acid, which prevents it from deteriorating under the influence of moisture during the rather long time which elapses, especially in the manufacture of torpedoes, before it becomes fully dry.

Mixtures of potassium chlorate and red phosphorus explode from shock *and from fire.* They do not burn in an orderly fashion as do black powder and most other pyrotechnic mixtures. No scrap or waste ought ever to be allowed to accumulate in the building where caps are made; it ought to be removed hourly, whether moist or not, and taken to a distance and thrown upon a fire which is burning actively.

### Silver Torpedoes

These contain silver fulminate, a substance which is as sensitive as the red phosphorus and chlorate mixture mentioned above, but which, however, is somewhat more predictable. They are made by the use of a *torpedo board,* that is, a board, say 7/8 inch thick, through which 3/4-inch holes have been bored. A 2-inch square of tissue paper is placed over each hole and punched into the hole to form a paper cup. A second board of the same thickness, the *gravel board,* has 1/2-inch holes, bored not quite through it, in number and position corresponding to the holes in the torpedo board. Fine gravel, free from dust, is poured upon it; the holes are filled, and the excess removed. The torpedo board, filled with paper cups, is inverted and set down upon the gravel board, the holes matching one another. Then the two boards, held firmly together, are turned over and set down upon the bench. The gravel falls down into the paper cups, and the gravel board is removed. A small amount of silver fulminate is now put, on top of the gravel, into each of the paper cups. This is a dangerous operation, for the act of picking up some of the fulminate with a scoop may cause the whole of it to explode. The explosion will be accompanied by a loud noise, by a flash of light, and by a tremendous local disturbance damaging to whatever is in the immediate neighborhood of the ful-

minate but without effect upon objects which are even a few inches away.

In one plant which the present writer has visited, the fulminate destined to be loaded into the torpedoes rests in a small heap in the center of a piece of thin rubber (dentist's dam) stretched over a ring of metal which is attached to a piece of metal weighing about a pound. This is held in the worker's left hand, and a scoop made from a quill, held in the right hand, is used to take up the fulminate which goes into each torpedo. If the fulminate explodes, it destroys the piece of stretched rubber—nothing else. And the rubber, moreover, cushions it so that it is less likely to explode anyway. The pound of metal is something which the worker can hold much more steadily than the light-weight ring with its rubber and fulminate, and it has inertia enough so that it is not jarred from his hand if an explosion occurs. After the fulminate has been introduced into the paper cups, the edges of each cup are gathered together with one hand and twisted with the thumb and forefinger of the other hand which have been moistened with paste. This operation requires care, for the torpedo is likely to explode in the fingers if it is twisted too tightly.

Torpedoes, whether silver, Japanese, or globe, ought to be packed in sawdust for storage and shipment, and they ought not to be stored in the same magazine or shipped in the same package with other fireworks. If a number of them are standing together, the explosion of one of them for any reason is practically certain to explode the others. Unpacked torpedoes ought not to be allowed to accumulate in the building in which they are made.

### Japanese Torpedoes

The so-called Japanese torpedoes appear to be an American invention. They contain a paper cap placed between two masses of gravel, and in general require to be thrown somewhat harder than silver torpedoes to make them explode. The same torpedo board is used as in the manufacture of silver torpedoes, but a gravel board which holds only about half as much gravel. After the gravel has been put in the paper cups, a paper cap, still moist, is placed on top of it, more gravel, substantially equal in amount to that already in the cup, is added to each, and the tops are twisted.

## Globe Torpedoes[50]

Small cups of manila paper, about ¾ inch in diameter and ⅞ inch deep, are punched out by machine. They are such that two of them may be fitted together to form a box. The requisite amount of powdered potassium chlorate is first introduced into the cups; then, on top of it and without mixing, the requisite

FIGURE 34. Manufacture of Globe Torpedoes. Introducing gravel and closing the paper capsules. (Courtesy National Fireworks Company and the *Boston Globe*.)

amount, already mixed, of the other components of the flash fulminating mixture is added. These other components are antimony sulfide, lampblack, and aluminum. Without disturbing the white and black powders in the bottoms of the cups, workers then fill the cups with clean coarse gravel and put other cups down upon them to form closed ¾ by ¾ inch cylindrical boxes. The little packages are put into a heated barrel, rotating at an angle with the horizontal, and are tumbled together with a solution of water-glass. The solution softens the paper (but later

[50] U. S. Pats. 1,199,775, 1,467,755, 1,783,999.

hardens it), and the packages assume a spherical shape. Small discs of colored paper (punchings) are added a few at a time until the globes are completely covered with them and have lost all tendency to stick together. They are then emptied out of the

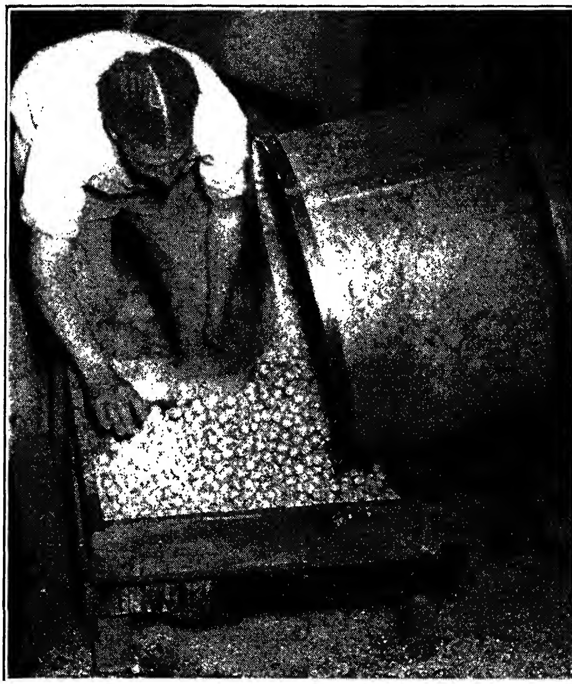


FIGURE 35. Manufacture of Globe Torpedoes. Removing the moist spheres from the tumbling barrel. (Courtesy National Fireworks Company and the *Boston Globe*.)

tumbler, dried in steam-heated ovens, and packed in wood shavings for storage and shipment.

## Railway Torpedoes

A railway torpedo consists of a flat tin box, of about an ounce capacity, filled with a fulminating composition and having a strip of lead, soldered to it, which may be bent in order to hold it in place upon the railroad track. It explodes when the first wheel of the locomotive strikes it, and produces a signal which is audible to the engineer above the noise of the train. Railway tor-

pedoes were formerly filled with compositions containing chlorate and red phosphorus, similar to those which are used in toy caps; but these mixtures are dangerous and much more sensitive than

FIGURE 36. Packing Globe Torpedoes in Wood Shavings. (Courtesy National Fireworks Company and the *Boston Globe.*)

is necessary. At present, safer perchlorate mixtures without phosphorus are used. The following compositions (Allen F. Clark) can be mixed dry and yield railway torpedoes which will not explode from ordinary shock or an accidental fall.

| | | |
|---|---|---|
| Potassium perchlorate | 6 | 12 |
| Antimony sulfide | 5 | 9 |
| Sulfur | 1 | 3 |

### English Crackers or Grasshoppers

These devices are old; they were described by John Bate and by Hanzelet Lorrain. English crackers are represented in the lower right-corner of Figure 23, reproduced from Lorrain's book of 1630. They are used in bombshells and, as Lorrain used them, in rockets, where they jump about in the air producing a series of flashes and explosions. Children shoot them on the ground like firecrackers where their movements suggest the behavior of grasshoppers.

English crackers are commonly loaded with granulated gunpowder, tamped into paper pipes like those from which pinwheels are made. The loaded pipes are softened by moisture in the same way, passed between rollers to make them flatter, folded in frames, and, for the best results, tied each time they are folded and then tied over the whole bundle. They are generally supplied with black match for lighting. They produce as many explosions as there are ligatures.

### Chinese Firecrackers

Firecrackers have long been used in China for a variety of ceremonial purposes. The houseboat dweller greets the morning by setting off a bunch of firecrackers, for safety's sake in an iron kettle with a cover over it, to keep all devils away from him during the day. For their own use the Chinese insist upon firecrackers made entirely of red paper, which leave nothing but red fragments, for red is a color particularly offensive to the devils. Firecrackers for export, however, are commonly made from tubes of cheap, coarse, brown paper enclosed in colored wrappers. Thirty years ago a considerable variety of Chinese firecrackers was imported into this country. There were "Mandarin crackers," made entirely from red paper and tied at the ends with silk thread; cheaper crackers plugged at the ends with clay (and these never exploded as satisfactorily); "lady crackers," less than an inch long, tied, and no thicker than a match stem; and "cannon crackers," tied with string, 6, 8, and 12 inches long, made of brown paper with brilliant red wrappers. All these were loaded with explosive mixtures of the general nature of black powder, were equipped with fuses of tissue paper twisted around black powder, and were sold, as Chinese firecrackers are now sold, in bunches with their fuses braided together. The composi-

tion 4 parts potassium nitrate, 1 of charcoal, and 1 of sulfur has been reported in Chinese firecrackers; more recently mixtures containing both potassium nitrate and a small amount of potassium chlorate have been used; and at present, when the importation of firecrackers over 1¾ inches in length is practically[51] prohibited, flash powders containing aluminum and potassium

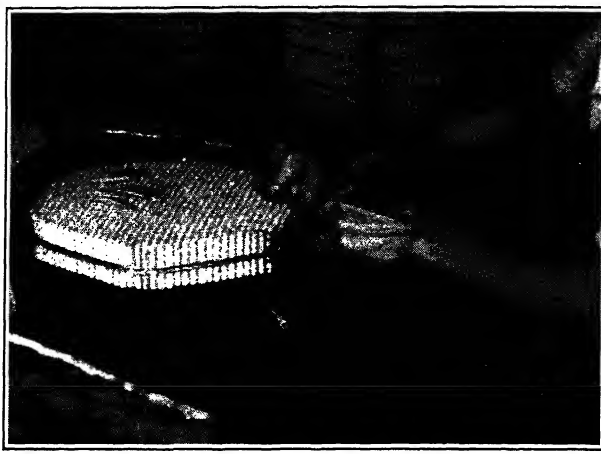


FIGURE 37. Chinese Firecrackers. Tying the Tubes into Bundles. (Courtesy Wallace Clark.)

chlorate are commonly used, for they give a sharper explosion than black powder.

The Chinese firecracker industry formerly centered in Canton but, since the Japanese occupation, has moved elsewhere, largely to French Indo-China and Macao in Portuguese territory. Its processes require great skill and manual dexterity, and have long been a secret and a mystery to Europeans. So far as we know, they had not been described in English print until Weingart's book[52] published an account of the manufacture of clay-plugged crackers based upon information received from the manager of a fireworks company at Hong Kong. His account is illustrated with three pen sketches, two of them of workmen

[51] Firecrackers not exceeding 1¾ inches in length and 5/16 inch in diameter carry a duty of 8 cents per pound. For longer crackers the duty is 25 cents per pound, which practically prohibits their importation.

[52] *Op. cit.*, pp. 166-170.

carrying out manual operations and a third which shows some of the tools and instruments. The brief account which follows is

FIGURE 38. Crimping the Back Ends of the Tubes. (Courtesy Wallace Clark.)

based upon conversations with Wallace Clark of Chicago and upon still and moving pictures which he took at a large factory in French Indo-China in January, 1939.

FIGURE 39. Punching Holes for Loading. (Courtesy Wallace Clark.)

The tubes for the firecrackers are rolled and cut to length in outlying villages, and are brought to the factory for loading.

They are tied in hexagonal bundles, Figure 37, each containing 1006 tubes. Since the twine tied tightly around the bundle

FIGURE 40. Loading. Filling the Tubes with Powder. (Courtesy Wallace Clark.)

crushes the 6 tubes at the corners of the hexagon, and since these are discarded, each bundle contains tubes for 1000 finished crackers.

FIGURE 41. Fusing and Crimping. (Courtesy Wallace Clark.)

The back ends of the crackers are then crimped; Figure 38. A bamboo stick is placed against the end of the tube and is

struck a sharp blow; this forces some of the paper down into the tube and closes it effectively. The operation, like all the other

FIGURE 42. Making the Fuse. (Courtesy Wallace Clark.)

operations in the manufacture of the crackers, is carried out very rapidly.

FIGURE 43. Making the Crackers into Bunches by Braiding Fuses Together. (Courtesy Wallace Clark.)

A sheet of paper is then pasted over the other side of the hexagonal bundle of tubes, closing the ends which are later to

carry the fuses. When this is dry, holes corresponding to the tubes are punched in the paper. The operation is carried out by young girls who punch the holes four at a time by means of four bamboo sticks held in one hand while they hold the bundle of tubes steady with the other; Figure 39. The edges of the paper are then bent slightly upward, giving it the form of a shallow saucer with 1000 holes in its bottom. The powder for charging the crackers is then introduced into this saucer, and the whole is

FIGURE 44. Wrapping the Bunches. (Courtesy Wallace Clark.)

shaken gently until all the tubes are full; Figure 40. Then, by a deft movement of the worker's hands and wrists, the excess powder in the saucer, and a portion of the powder in each of the tubes, is emptied out quickly, each of the tubes being left partly full of powder with enough empty space at the top for the fuse and the crimp. This operation, of all those in the manufacture, is considered to be the one which requires the greatest skill. Day after day the average consumption of powder per 1000 or per 100,000 crackers is remarkably constant.

The paper is then torn off from the hexagonal bundle, and the fuses, cut to length, are put in place by one workman while another with a pointed bamboo stick rapidly crimps the paper around them; Figure 41. The fuse is made from narrow strips of tissue paper about 2 feet long. While one end of the strip is clamped to the bench and the other is held in the hand, the strip

is shaped by a motion of the worker's other hand into the form of a trough which is then filled with a narrow train of powder, and, by another motion of the hand, the fingers being moistened, is twisted into the finished fuse; Figure 42. This is set aside to dry and is cut into lengths for use in the crackers. The fuses of the finished crackers are braided or pleated together, Figure 43, making the crackers into bunches, and the bunches are wrapped and labeled, Figure 44.

## Flash Cracker Composition

Chinese firecrackers and American machine-made salutes are loaded with compositions which contain powdered aluminum and potassium chlorate or perchlorate. They produce a bright flash and an extremely sharp report when they explode. The compositions listed below are typical. The first four in the table have been used in Chinese firecrackers. For the last four the author is indebted to Allen F. Clark.

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Potassium perchlorate | .. | .. | .. | .. | 6 | 1 | 7 | .. |
| Potassium chlorate | 2 | 3 | .. | 7 | .. | .. | .. | .. |
| Potassium nitrate | .. | .. | 5 | .. | .. | .. | .. | .. |
| Barium nitrate | .. | .. | .. | .. | 3 | 1 | .. | 4 |
| Aluminum (fine powder) | 1 | 4 | 2 | 1 | 5 | 1 | 5 | 2 |
| Sulfur | 1 | 3 | 3 | 2 | .. | 1 | .. | 1 |
| Antimony sulfide | .. | .. | .. | 1 | .. | .. | .. | .. |

The compositions which contain barium nitrate produce a green flash, the others a white one. All of them burn with great rapidity in the open. It is debatable whether the phenomenon of the burning is not really an explosion, or would be one if the material were not allowed to scatter while being burned. With the exception of the third and the last, they are all fulminating explosives when confined. All the mixtures which contain sulfur along with chlorate or perchlorate can be exploded on an iron anvil by a moderately strong blow with an iron hammer.

## Sparklers

Snowball sparklers (Allen F. Clark) are made from:

| | |
|---|---|
| Potassium nitrate | 64 |
| Barium nitrate | 30 |
| Sulfur | 16 |
| Charcoal dust | 16 |
| Antimony sulfide | 16 |
| Fine aluminum powder | 9 |
| Dextrin | 16 |

The ingredients are all powdered to pass a 200-210 mesh sieve. The dry materials are mixed thoroughly and sifted, then moistened little by little with water with thorough mixing until the mixture attains the consistency of heavy molasses. Iron wires (20 gauge) of convenient length are dipped in the mixture and are hung up to dry for 24 hours. These are dipped a second time for size, and allowed to dry for another 24 hours. The sparklers burn with a bright white light and throw out "soft sparks" from the charcoal and occasionally scintillating sparks from the burning of the iron wire.

Other mixtures which produce similar effects are as follows:

| | | |
|---|---|---|
| Potassium nitrate | 64 | .. |
| Potassium perchlorate | 3 | 16 |
| Barium nitrate | .. | 6 |
| Sulfur | 18 | 4 |
| Lampblack | 5 | .. |
| Red gum | 4 | 4 |
| Fine aluminum powder | 6 | 6 |
| Coarse aluminum powder | .. | 4 |

The first of these burns with a lilac-colored flame as contrasted with the flame of the second which appears white. These compositions are applied by adding the intimately mixed dry ingredients to a liquid known as "black wax," procured by melting together 3 pounds of rosin and 1 gallon of liquid roofing-paper tar. The iron wires are dipped two or three times in the resulting slurry, and allowed to dry between dips.

The use of iron and steel filings in the compositions produces a more brilliant display of scintillating sparks. The following formulas are typical. Water is used for applying the compositions. The iron and steel filings which are used in these compositions are coated, before the mixing, with paraffin or linseed oil to protect them from rusting.

| | | | |
|---|---|---|---|
| Barium nitrate | 48 | 48 | .. |
| Potassium perchlorate | .. | .. | 6 |
| Fine aluminum powder | 7 | 7 | 1 |
| Fine iron filings | 24 | 18 | .. |
| Fine steel filings | .. | 9 | 12 |
| Manganese dioxide | 2 | 1 | .. |
| Dextrin | 12 | 12 | 2 |
| Glucose | .. | 1 | .. |

## Wire Dips and Colored Fire Sticks

These devices are made in the same way as sparklers, by dipping wires or twisted narrow strips of iron or thin sticks of wood, and generally burn with a tranquil flame except for the sparks that come from the burning of the iron wire or strip. Several typical compositions are listed. Alcohol is used for applying the

| | Red | | | Green | White |
|---|---|---|---|---|---|
| Potassium chlorate | .. | 2 | 3 | .. | .. |
| Potassium perchlorate | .. | .. | .. | .. | 10 |
| Strontium nitrate | 5 | 6 | 16 | .. | .. |
| Barium chlorate | .. | .. | .. | 16 | .. |
| Fine aluminum powder | .. | .. | .. | .. | 7 |
| Coarse aluminum powder | .. | 6 | .. | 24 | .. |
| Shellac | 1 | 1 | .. | 3 | .. |
| Red gum | .. | .. | 4 | .. | .. |
| Dextrin | .. | .. | 3 | .. | 3 |

compositions which contain shellac; water, for applying the others which contain dextrin.

## Pharaoh's Serpents[53]

Wöhler in 1821 first reported the remarkable property of mercurous thiocyanate that it swells up when it is heated, "winding out from itself at the same time worm-like processes, to many times its former bulk, of a very light material of the color of graphite, with the evolution of carbon disulfide, nitrogen, and mercury." Mercuric thiocyanate, which gives better snakes than the mercurous compound, came early into use for this purpose in pyrotechnic toys. When a heap or pellet of either of these compounds is set on fire, it burns with an inconspicuous blue flame, producing sulfur dioxide and mercury vapor. The resulting pale brown or pale gray snake, if broken, is found to be much darker in the interior, and evidently consists of paracyanogen and mercuric sulfide, the mercury having been burned and vaporized from the outer layer.

Mercuric thiocyanate is prepared by adding a solution of

[53] Cf. Davis, article entitled "Pyrotechnic Snakes," in *J. Chem. Education*, 17, 268-270 (1940).

potassium, sodium, or ammonium thiocyanate to a solution of mercuric nitrate, a ferric chloride or ferric alum indicator being used to indicate by a red color when enough of the former solution has been added. This is necessary since mercuric thiocyanate is soluble in an excess of either of the reagents by the interaction of which it is produced. The precipitate is collected, washed, dried, powdered, moistened with gum-arabic water in which a little potassium nitrate is dissolved, and made into small pellets by means of a device like a star board or by a pelleting machine. The small pellets are known as *Pharaoh's serpent's eggs.*

*Snakes-in-the-grass, volcano snakes,* etc., depend upon the use of ammonium dichromate. If this material in the form of a powder is made into a conical heap, and a flame applied to the top of it, a visible but not violent "combustion" proceeds through the mass, which "boils up" to form a large volume of green material resembling tea leaves.

$$(NH_4)_2Cr_2O_7 \qquad N_2 + 4H_2O + Cr_2O_3$$

In practice, more flame is desired than ammonium dichromate alone will give. Weingart[54] recommends a mixture of 2 parts of ammonium dichromate with 1 of potassium nitrate and 1 of dextrin. Tinfoil cones are made from circles of tinfoil shaped on a former, and are introduced by means of the former into conical cavities in a block of wood; they are then about half filled with the powdered mixture, a Pharaoh's serpent's egg is pressed in, and the edges of the tinfoil are turned down upon it to form the base of the cone.

While the fumes from burning mercuric thiocyanate are offensive because of their sulfur dioxide, the small amount of mercury vapor which they contain probably presents no serious danger. The possibility, however, that children may swallow the pellets, with fatal consequences, is a real hazard. For this reason, the sale of mercury snakes has been forbidden by law in many states, and black non-mercury snakes, which are essentially non-poisonous, have come into general use.

### Black Non-Mercury Snakes[55]

These are used in the form of *barrel snakes, hat snakes* (black

[54] *Op. cit.,* p. 152.
[55] Davis, *loc. cit.*

pellets affixed to black discs of pasteboard to form what look like miniature broad-brimmed black hats), *colored fire snakes*, etc. The best which we have seen are prepared from naphthol pitch by a process described by Weingart.[56] The naphthol pitch is a by-product in the manufacture of $\beta$-naphthol. The method of "nitration by kneading" is so unusual that it appears worth while to describe the process in detail.

*Preparation of Black Non-Mercury Snakes.* Thirty grams of powdered naphthol pitch is mixed intimately with 6 grams of linseed oil, and the material is chilled in a 200-cc. Pyrex beaker surrounded by cracked ice. Twenty-one cubic centimeters of fuming nitric acid (*d.* 1.50) is added in small portions, one drop at a time at first, and the material is stirred over, kneaded, and kept thoroughly mixed at all times by means of a porcelain spatula. The addition of each drop of acid, especially at the beginning of the process, causes an abundance of red fumes, considerable heating, and some spattering. It is recommended that goggles and rubber gloves be worn, and that the operation be carried out in an efficient hood. The heat of the reaction causes the material to assume a plastic condition, and the rate of addition of the acid ought to be so regulated that this condition is maintained. After all the acid has been added, the dark brown, doughlike mass becomes friable on cooling. It is broken up under water with the spatula, washed thoroughly, and allowed to dry in the air. The product is ground up in a porcelain mortar with 10.5 grams of picric acid, made into a moist meal with gum-arabic water, pelleted, and dried. A pellet ½ inch long and ⅜ inch in diameter gives a snake about 4 feet long, smooth-skinned and glossy, with a luster like that of coke, elastic, and of spongy texture within.

The oxidized linseed oil produced during the nitration appears to play an important part in the formation of the snakes. If naphthol pitch alone is nitrated, ground up with picric acid, and made into pellets after moistening with linseed oil, the pellets when fresh do not yield snakes, but do give snakes after they have been kept for several months, during which time the linseed oil oxidizes and hardens. Weingart states in a letter that he has obtained satisfactory results by using, instead of naphthol pitch, the material procured by melting together 60 parts of Syrian asphalt and 40 of roofing pitch. Worked up in the regular way this "yielded fairly good snakes which were improved by rubbing

[56] *Op. cit.*, p. 153.

the finished product up with a little stearine before forming into pellets." The present writer has found that the substitution of $\beta$-naphthol for naphthol pitch yields fairly good snakes which, however, are not so long and not so shiny, and are blacker and covered with wartlike protuberances.

## Smokes

*Smoke shells* and rockets are used to produce *smoke clouds* for military signaling and, in daylight fireworks, for ornamental effects. The shell case or rocket head is filled with a fine powder of the desired color, which powdered material need not necessarily be one which will tolerate heat, and this is dispersed in the form of a colored cloud by the explosion of a small bag of gunpowder placed as near to its center as may be. Artificial vermilion (red), ultramarine (blue), Paris green, chrome yellow, chalk, and ivory black are among the materials which have been used, but almost any material which has a bright color when powdered and which does not cake together may be employed.

*Colored smokes* strictly so called are produced by the burning, in *smoke pots* or smoke cases, of pyrotechnic compositions which contain colored substances capable of being sublimed without an undue amount of decomposition. The substances are volatilized by the heat of the burning compositions to form colored vapors which quickly condense to form clouds of finely divided colored dust. Colored smokes are used for military signaling, and recently have found use in colored moving pictures. Red smokes, for example, were used in the "Wizard of Oz." Colored smoke compositions are commonly rammed lightly, not packed firmly, in cases, say 1 inch in internal diameter and 4 inches long, both ends of which are closed with plugs of clay or wood. Holes, ¼ inch in diameter, are bored through the case at intervals on a spiral line around it; the topmost hole penetrates well into the composition and is filled with starting fire material into which a piece of black match, held in place by meal powder paste, is inserted. According to Faber,[57] the following-listed compositions were used in American airplane smoke-signal grenades during the first World War.

[57] *Op. cit.*, Vol. 1, p. 219.

| | Red | Yellow | Green | Blue |
|---|---|---|---|---|
| Potassium chlorate | 1 | 33 | 33 | 7 |
| Lactose | 1 | 24 | 26 | 5 |
| Paranitraniline red | 3 | .. | .. | .. |
| Auramine | .. | 34 | 15 | .. |
| Chrysoidine | .. | 9 | .. | .. |
| Indigo | .. | .. | 26 | 8 |

The following (Allen F. Clark) are illustrative of the perchlorate colored smoke compositions which have come into use more recently.

| | Red | Green | Blue |
|---|---|---|---|
| Potassium perchlorate | 5 | 6 | 5 |
| Antimony sulfide | 4 | 5 | 4 |
| Rhodamine red | 10 | .. | .. |
| Malachite green | .. | 10 | .. |
| Methylene blue | .. | .. | 10 |
| Gum arabic | 1 | 1 | 1 |

Many other dyestuffs may be used. Paranitraniline Yellow gives a canary yellow smoke, and Flaming Red B gives a crimson-colored smoke by comparison with which the smoke from Paranitraniline Red appears to be scarlet. None of the colored smoke compositions are adapted to indoor use. All the smokes are unpleasant and unwholesome.

*White smoke* is produced by burning a mixture of potassium chlorate 3 parts, lactose 1, and finely powdered ammonium chloride 1. The smoke, which consists of finely divided ammonium chloride, is not poisonous, and has found some use in connection with the study of problems in ventilation.

For use in trench warfare, for the purpose of obscuring the situation from the sight of the enemy, a very satisfactory dense *white* or *gray smoke* is procured by burning a mixture of zinc dust and hexachloroethane. The mixture requires a strong starting fire. The smoke consists largely of finely divided zinc chlo-

ride. For a grayer smoke naphthalene or anthracene is added to the mixture. Torches for *black smoke* have also been used, charged with a mixture of potassium nitrate and sulfur with rosin or pitch and generally with such additional ingredients as sand, powdered chalk, or glue to modify the rate of their burning.

When shells are loaded with certain high explosives which produce no smoke (such as amatol), *smoke boxes* are generally inserted in the charges in order that the artilleryman, by seeing the smoke, may be able to judge the position and success of his fire. These are cylindrical pasteboard boxes containing a mixture of arsenious oxide and red phosphorus, usually with a small amount of stearine or paraffin.

# CHAPTER IV

## AROMATIC NITRO COMPOUNDS

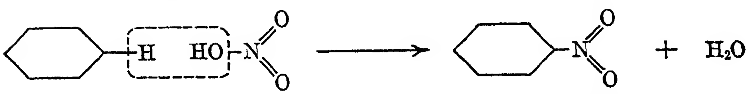
Aromatic nitro compounds are generally stable but are frequently reactive, especially if they contain groups other than nitro groups in the *meta* position with respect to one another. As a class they constitute the most important of the military high explosives. They are also used as components of smokeless powder, in compound detonators, and in primer compositions. Liquid nitro compounds, and the mixtures which are produced as by-products from the manufacture of pure nitro compounds for military purposes, are used in non-freezing dynamite and other commercial explosives. The polynitro compounds are solvents for nitrocellulose.

The nitro compounds are poisonous. Nitrobenzene, known also as "oil of mirbane," is absorbed through the skin and by breathing its vapors, and has been reported to cause death by the careless wearing of clothing upon which it had been spilled. The less volatile polynitro compounds, like trinitrotoluene, are absorbed through the skin when handled, and may cause injury by the inhalation of their dust or of their vapors when they are melted. Minor TNT sickness may manifest itself by cyanosis, dermatitis, nose bleeding, constipation, and giddiness; the severer form, by toxic jaundice and aplastic anemia.[1] One of the nitro groups is reduced in the body, and dinitrohydroxylaminotoluene may be detected in the urine. Trinitrobenzene is more poisonous than trinitrotoluene, which, in turn, is more poisonous than trinitroxylene, alkyl groups in this series having the same effect as in the

[1] J. W. Schereschewsky, "Trinitrotoluol, Practical Points in Its Safe Handling," U. S. Pub. Health Service, Reprint 434 from *Pub. Health Repts.*, Nov. 16, 1917, pp. 1919-1926. C. Voegtlin, C. W. Hooper, and J. M. Johnson, "Trinitrotoluene Poisoning—Its Nature, Diagnosis and Prevention," U. S. Pub. Health Service, *Hyg. Lab. Bull. 126,* 1920. A. Hamilton, "Trinitrotoluene as an Industrial Poison," *J. Ind. Hyg.,* 3, 102-119 (1921). A. L. Leigh Silver, "Treatment and Prevention of Industrial Diseases in Filling Factories," *J. Roy. Army Med. Corps,* July, 1938, pp. 87-96.

phenols, cresol, xylenol, etc., where they reduce the toxicity of the substances but increase their antiseptic strength.

In the manufacture of explosives the nitro groups are always introduced by the direct action of nitric acid on the aromatic substances. The simple reaction involves the production of water and is promoted by the presence of sulfuric acid which thus functions as a dehydrating agent. We shall later see cases in which sulfuric acid is used as a means of hindering the introduction of nitro groups. In consequence of the reaction, the nitrogen




atom of the nitro group becomes attached to the carbon atom of the aromatic nucleus. Nitro groups attached to the nucleus, unless *ortho* and *para* to other nitro groups, are not affected by sulfuric acid as are nitro groups attached to oxygen (in nitric esters) and to nitrogen (in nitroamines), or, ordinarily, by hydrolytic agents as are nitro groups attached to oxygen. Nitric acid is a nitrating agent both at low and at elevated temperatures; its vigor in this respect depends upon the concentration. But it is an oxidizing agent even in fairly dilute solution, and becomes more vigorous if the temperature is raised. Further, it decomposes when heated to produce nitrous acid, which is also a powerful oxidizing agent and may reduce the yield of the desired product. Nitrous acid present in the nitrating acid may also result in the formation of nitrophenols from aromatic amines. Aromatic nitro compounds, such as TNT and picric acid, on refluxing for some hours with nitric acid (*d.* 1.42) and then distilling the mixture, yield appreciable quantities of tetranitromethane, formed by the rupture of the ring and the nitration of the individual carbon atoms. The nitro group "strengthens" the ring against attack by acid oxidizing agents, but makes it more accessible to attack by alkaline ones. The polynitro compounds are destroyed rapidly by warm alkaline permanganate yielding oxalic acid. They combine with aniline, naphthylamine, etc., to form brightly colored molecular compounds. All aromatic nitro compounds give colors, yellow, orange, red, even purple, with alkaline reagents.

The position which the nitro group takes on entering the aromatic nucleus and the ease with which the substitution is accomplished depend upon the group or groups already present

on the nucleus. We are accustomed to speak of the orienting or directing effect of the groups already present and of their influence in promoting or inhibiting further substitution. The two simple rules which summarize these effects have important implications and wide applications in the chemistry of aromatic substances.

## Effect of Groups on Further Substitution

1. ORIENTING EFFECT. *The Modified Rule of Crum Brown and Gibson.* If the atom attached to the aromatic nucleus is attached to some other atom by an unsaturated linkage (i.e., by any bond which we commonly write as double or triple), then the next entering group takes the *meta* position; otherwise it takes the *ortho* and *para* positions.

The rule relieves us of the necessity for remembering which groups orient *meta* and which *ortho-para*; we may write them down on demand, thus: the $—NO_2$, —NO, —CO—, —COOH, —CHO, $—SO_2—OH$, —CN groups orient *meta*; and the $—NH_2$, —NHR, $—NR_2$, —OH, —OR, $—CH_3$, $—CH_2–CH_3$, —Cl, —Br groups orient *ortho-para*. It is necessary, however, to take note of three or four exceptions, only one of which is important in the chemistry of explosives, namely, that the azo group, —N=N—, orients *ortho-para*; the trichloromethyl group, $—CCl_3$, *meta*; that such conjugate systems as occur in cinnamic acid, —CH=CH—CO—, orient *ortho-para*; and further that a large excess of strong sulfuric acid reverses to a greater or less extent the normal orienting effects of the methoxy and ethoxy groups, of the amino group wholly and of the monosubstituted and disubstituted amino groups in part.

In all discussions of the application of the rule we make reference to the principal products of the reaction; substitution occurs for the most part in accordance with the rule, or with the exceptions, and small amounts of other materials are usually formed as by-products. In the mononitration of toluene, for example, about 96 per cent of the product is a mixture of *o*- and *p*-nitrotoluene, and about 4 per cent is the *m*-compound. Under the influence of *ortho-para* orienting groups, substitution occurs in the two positions without much preference for either one, but it appears to be the case that, when nitro groups are introduced, low temperatures favor the formation of *p*-compounds. The effect

of temperature on sulfonations appears to be exactly the opposite.

2. Ease of Substitution. *Ortho-para* orienting groups promote substitution; *meta* orienting groups hinder it and make it more difficult. The rule may be stated otherwise: that substitution under the influence of *ortho-para* orienting groups occurs under less vigorous conditions of temperature, concentration of reagents, etc., than it does with the unsubstituted aromatic hydrocarbon itself; under the influence of *meta* orienting groups more vigorous conditions than with the unsubstituted hydrocarbon are necessary for its successful accomplishment. The rule may also be stated that *ortho-para* substitution is easier than *meta*. In this last form it fails to make comparison with substitution in the simple hydrocarbon, but does point clearly to the implication, or corollary, that the orienting effect of an *ortho-para* orienting group dominates over that of one which orients *meta*. To the rule in any of these forms, we must add that, when more than one group is already present on the nucleus, the effect of the groups is additive.

Toluene nitrates more easily than benzene; aniline and phenol more easily still. Higher temperature and stronger acid are needed for the introduction of a second nitro group into benzene than for the introduction of the first, for the second is introduced under the influence of the *meta*-orienting first nitro group which tends to make further substitution more difficult. The inhibitory effect of two nitro groups is so great that the nitration of dinitrobenzene to the trinitro compound is extremely difficult. It is more difficult to nitrate benzoic acid than to nitrate nitrobenzene. The common experience of organic chemists indicates that the order of the groups in promoting substitution is about as follows:

$$—OH > —NH_2 > —CH_3 > —Cl > —H > —NO_2 > —SO_2(OH) > —COOH$$

Any one of these groups makes substitution easier than the groups which are printed to the right of it.

Xylene nitrates more easily than toluene. Two methyl groups promote substitution more than one methyl group does, and this appears to be true whether or not the methyl groups agree among themselves in respect to the positions which they activate. Although a nitro group may be said to "activate" a particular position, inasmuch as it points to that position as the one in which substitution will next occur, it nevertheless makes substitution more difficult in that position, as well as in all other positions on

the nucleus. The nitroanilines are more difficult to nitrate than aniline because of their inhibiting nitro group, and more easy to nitrate than nitrobenzene because of their promoting amino group. In *o*- and *p*-nitroaniline the amino and nitro groups agree in activating the same positions, and both substances yield 2,4,6-trinitroaniline when they are nitrated. In *m*-nitroaniline, the nitro group "activates" the 5-position, while the amino group activates the 2-, 4-, and 6-positions. Nitration takes place under the influence of the *ortho-para*-orienting amino group, and 2,3,4,6-tetranitroaniline results.

### Utilization of Coal Tar

The principal source of aromatic compounds is coal tar, produced as a by-product in the manufacture of coke. Gas tar, of which much smaller quantities are produced, also contains these same materials. Aromatic hydrocarbons occur in nature in Borneo and other petroleums, and they may be prepared artificially by stripping hydrogen atoms from the cycloparaffins which occur in Caucasus petroleum and elsewhere. They are also produced from paraffin hydrocarbons by certain processes of cracking, and it is to be expected that in the future aromatic compounds will be produced in increasing quantity from petroleum which does not contain them in its natural state.

Coal yields about 6 per cent of its weight of tar. One ton of tar on distillation gives:

Light Oil—yielding about 32 lb. of benzene, 5 lb. of toluene, and 0.6 lb. of xylene.

Middle Oil—yielding about 40 lb. of phenol and cresols, and 80-120 lb. of naphthalene.

Heavy Oil—yielding impure cresols and other phenols.

Green Oil—yielding 10-40 lb. of anthracene.

Pitch—1000-1200 lb.

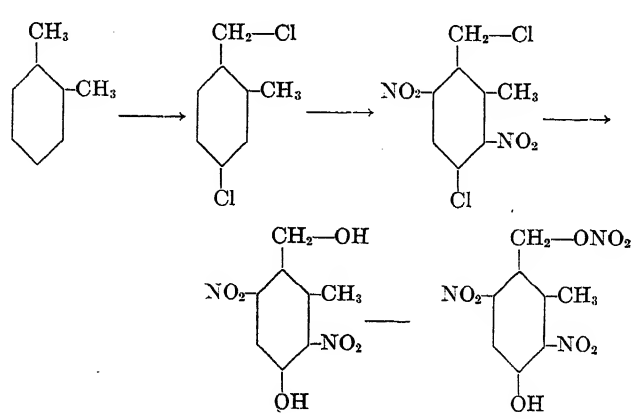
Naphthalene is the most abundant pure hydrocarbon obtained from coal tar. It takes on three nitro groups readily, and four under vigorous conditions, but ordinarily yields no product which is suitable by itself for use as an explosive. Nitrated naphthalenes, however, have been used in smokeless powder and, when mixed with ammonium nitrate and other materials, in high explosives for shells and for blasting.

The phenol-cresol fraction of coal tar yields phenol on distillation, which is convertible to picric acid, and the cresols, of which

*m*-cresol is the only one which yields a trinitro derivative directly. Moreover, synthetic phenol from benzene, through chlorobenzene by the Dow process, is purer and probably cheaper in times of stress.

Of the hydrocarbons toluene is the only one which nitrates sufficiently easily and yields a product which has the proper physical and explosive properties. Trinitrotoluene is the most widely used of the pure aromatic nitro compounds. It melts at such temperature that it can be loaded by pouring. It is easily and surely detonated, and is insensitive to shock, though not insensitive enough to penetrate armor-plate without exploding until afterwards. It is powerful and brisant, but less so than trinitrobenzene which would offer certain advantages if it could be procured in sufficient quantity.

Of the xylenes, the *meta* compound yields a trinitro derivative more readily than toluene does, but trinitro-*m*-xylene (TNX) melts somewhat higher than is desirable and is not quite powerful enough when used alone. It has been used in shells in mixtures with TNT and with ammonium nitrate. The other xylenes yield only dinitro derivatives by direct nitration. A mixture of *o*- and *p*-xylene may be converted into an explosive—an oily mixture of a large number of isomers, which has been used in the composition of non-freezing dynamites—by chlorinating at an elevated temperature in the presence of a catalyst (whereby chlorine is substituted both in the side chain and on the nucleus), then nitrating, then hydrolyzing (whereby both chlorines are replaced by hydroxyl groups, the nuclear chlorine being activated by the nitro groups), and finally nitrating once more.



In each step several isomers are formed—only one of the possibilities in each case is indicated above—and the *ortho* and *para* compounds both go through similar series of reactions. The product is too sensitive and in the wrong physical state (liquid) for use as a military explosive. In short, for the manufacture of

FIGURE 45. Marius Marqueyrol, Inspecteur-Général des Poudres, France, 1919. Author of many researches on aromatic nitro compounds, nitrocellulose, smokeless powder, stabilizers and stability, chlorate explosives, etc.—published for the most part in the *Mémorial des poudres* and in the *Bulletin de la société chimique de France.*

military explosives toluene is the most valuable of the materials which occur in coal tar.

In time of war the industries of a country strive to produce as much toluene as possible. The effort results in the production also of increased quantities of other aromatic hydrocarbons, particularly of benzene, and these become cheaper and more abundant. Every effort is made to utilize them profitably for military purposes. As far as benzene is concerned, the problem has been solved through chlorobenzene, which yields aniline and phenol by the Dow process, and hence picric acid, and which gives dinitrochlorobenzene on nitration which is readily convertible, as will be described later, into picric acid and tetryl and several other

explosives that are quite as necessary as TNT for military purposes.

## Effects of Substituents on Explosive Strength

Bomb experiments show that trinitrobenzene is the most powerful explosive among the nitrated aromatic hydrocarbons. One methyl group, as in TNT, reduces its strength; two, as in TNX, reduce it further; and three, as in trinitromesitylene, still further yet. The amino and the hydroxyl groups have less effect than the methyl group; indeed, two hydroxyl groups have less effect than one methyl—and trinitroresorcinol is a stronger explosive than TNT, though weaker than TNB. TNT is stronger than trinitrocresol, which differs from it in having an hydroxyl group. The figures given below were determined by exploding the materials, loaded at the density indicated, in a small bomb, and measuring the pressure by means of a piston and obturator. *Density of loading* is grams of explosive per cubic centimeter of bomb capacity.

| | Pressure: Kilograms per square centimeter | | |
|---|---|---|---|
| Density of loading: | 0.20 | 0.25 | 0.30 |
| Trinitrobenzene | 2205 | 3050 | 4105 |
| Trinitrotoluene | 1840 | 2625 | 3675 |
| Trinitro-*m*-xylene | 1635 | 2340 | 2980 |
| Trinitromesitylene | 1470 | 2200 | 2780 |
| Trinitrophenol (picric acid) | 2150 | 3055 | 3865 |
| Trinitroresorcinol (styphinic acid) | 2080 | 2840 | .... |
| Trinitroaniline (picramide) | 2080 | 2885 | 3940 |
| Trinitro-*m*-cresol | 1760 | 2480 | 3360 |
| Trinitronaphthalene | .... | 2045 | 2670 |

Similar inferences may be made from the results of lead block tests. Fifteen grams of the explosives produced the expansions indicated below, each figure representing the average from twenty or more experiments:

| | |
|---|---|
| Trinitrobenzene | 480 cc. |
| Trinitrotoluene | 452 cc. |
| Picric acid | 470 cc. |
| Trinitrocresol | 384 cc. |
| Trinitronaphthalene | 166 cc. |

### Mono- and Di-Nitrobenzene

Nitrobenzene is a pale yellow liquid, b.p. 208.0°, which is poisonous and has an almondlike odor closely resembling that of benzaldehyde (which is not poisonous). It is used as a component of certain Sprengel explosives and as a raw material for the preparation of aniline and of intermediates for the manufacture of dyestuffs and medicinals. Its preparation, familiar to every student of organic chemistry, is described here in order that the conditions for the substitution of one nitro group in benzene may serve us more conveniently as a standard for judging the relative ease and difficulty of the nitration of other substances.

*Preparation of Nitrobenzene.* One hundred and fifty grams of concentrated sulfuric acid (*d.* 1.84) and 100 grams of nitric acid (*d.* 1.42) are mixed in a 500-cc. flask and cooled to room temperature, and 51 grams of benzene is added in small portions at a time with frequent shaking. Shaking at this point is especially necessary lest the reaction suddenly become violent. If the temperature of the mixture rises above 50-60°, the addition of the benzene is interrupted and the mixture is cooled at the tap. After all the benzene has been added, an air condenser is attached to the flask and the material is heated in the water bath for an hour at 60° (thermometer in the water). After cooling, the nitrobenzene (upper layer) is separated from the spent acid, washed once with water (the nitrobenzene is now the lower layer), then several times with dilute sodium carbonate solution until it is free from acid, then once more with water, dried with calcium chloride, and distilled (not quite to dryness). The portion boiling at 206-208° is taken as nitrobenzene.

*m*-Dinitrobenzene, in accordance with the rule of Crum Brown and Gibson, is the only product which results ordinarily from the nitration of nitrobenzene. Small amounts of the *ortho* and *para* compounds have been procured, along with the *meta*, from the nitration of benzene in the presence of mercuric nitrate.[2] Dinitrobenzene has been used in high explosives for shells in mixtures with more powerful explosives or with ammonium nitrate. Its use

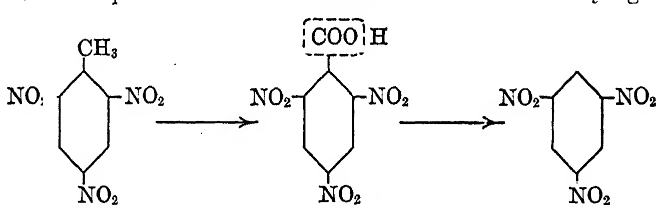
[2] Davis, *J. Am. Chem. Soc.*, 43, 598 (1921).

as a raw material for the manufacture of tetranitroaniline is now no longer important.

*Preparation of Dinitrobenzene.* A mixture of 25 grams of concentrated sulfuric acid (*d.* 1.84) and 15 grams of nitric acid (*d.* 1.52) is heated in an open flask in the boiling water bath in the hood, and 10 grams of nitrobenzene is added gradually during the course of half an hour. The mixture is cooled somewhat, and drowned in cold water. The dinitrobenzene separates as a solid. It is crushed with water, washed with water, and recrystallized from alcohol or from nitric acid. Dinitrobenzene crystallizes from nitric acid in beautiful needles which are practically colorless, m.p. 90°.

### Trinitrobenzene

1,3,5-Trinitrobenzene (*sym*-trinitrobenzene, TNB) may be prepared only with the greatest difficulty by the nitration of *m*-dinitrobenzene. Hepp[3] first prepared it by this method, and Hepp and Lobry de Bruyn[4] improved the process, treating 60 grams of *m*-dinitrobenzene with a mixture of 1 kilo of fuming sulfuric acid and 500 grams of nitric acid (*d.* 1.52) for 1 day at 100° and for 4 days at 110°. Claus and Becker[5] obtained trinitrobenzene by the action of concentrated nitric acid on trinitrotoluene. Trinitrobenzoic acid is formed first, and this substance in the hot liquid loses carbon dioxide from its carboxyl group.



For commercial production the Griesheim Chem. Fabrik[6] is reported to have used a process in which 1 part of TNT is heated at 150-200° with a mixture of 5 parts of fuming nitric acid and 10 parts of concentrated sulfuric acid. In a process devised by J. Meyer,[7] picryl chloride (2,4,6-trinitrochlorobenzene) is reduced by means of copper powder in hot aqueous alcohol. The reported details are 25 kilos of picryl chloride, 8 kilos of copper

[3] *Ber.*, **9**, 402 (1876); *Ann.*, **215**, 345 (1882).
[4] *Rec. trav. chim.*, **13**, 149 (1894).
[5] *Ber.*, **16**, 1597 (1883).
[6] Ger. Pat. 77,353, 77,559 (1893); 127,325 (1901).
[7] Ger. Pat. 234,726 (1909).

powder, 250 liters of 95 per cent alcohol, and 25 liters of water, refluxed together for 2 hours and filtered hot; the TNB crystallizes out in good yield when the liquid is cooled.

The nitration of *m*-dinitrobenzene is too expensive of acid and of heat for practical application, and the yields are poor. Toluene and chlorobenzene are nitrated more easily and more economically, and their trinitro compounds are feasible materials for the preparation of TNB. Oxidation with nitrosulfuric acid has obvious disadvantages. The quickest, most convenient, and cheapest method is probably that in which TNT is oxidized by means of chromic acid in sulfuric acid solution.

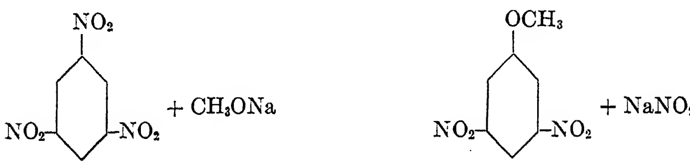
*Preparation of Trinitrobenzene.* A mixture of 30 grams of purified TNT and 300 cc. of concentrated sulfuric acid is introduced into a tall beaker, which stands in an empty agateware basin, and the mixture is stirred actively by means of an electric stirrer while powdered sodium dichromate ($Na_2Cr_2O_7 \cdot 2H_2O$) is added in small portions at a time, care being taken that no lumps are formed and that none floats on the surface of the liquid. The temperature of the liquid rises. When it has reached 40°, cold water is poured into the basin and the addition of dichromate is continued, with stirring, until 45 grams has been added, the temperature being kept always between 40° and 50°. The mixture is stirred for 2 hours longer at the same temperature, and is then allowed to cool and to stand over night, in order that the trinitrobenzoic acid may assume a coarser crystalline form and may be filtered off more readily. The strongly acid liquid is filtered through an asbestos filter; the solid material is rinsed with cold water and transferred to a beaker in which it is treated with warm water at 50° sufficient to dissolve all soluble material. The warm solution is filtered, and boiled until no more trinitrobenzene precipitates. The crystals of TNB growing in the hot aqueous liquid often attain a length of several millimeters. When filtered from the cooled liquid and rinsed with water, they are practically pure, almost colorless or greenish yellow leaflets, m.p. 121-122°.

Trinitrobenzene is only moderately soluble in hot alcohol, more readily in acetone, ether, and benzene. Like other polynitro aromatic compounds it forms colored molecular compounds with many aromatic hydrocarbons and organic bases.[8] The compound

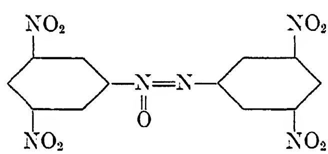
[8] Compare Hepp, *Ann.*, **215**, 356 (1882); Sudborough, *J. Chem. Soc.*, **75**, 588 (1889); **79**, 522 (1901); **83**, 1334 (1903); **89**, 583 (1906); **97**, 773 (1910); **99**, 209 (1911); **109**, 1339 (1916); Sachs and Steinert, *Ber.*, **37**, 1745 (1904); Nölting and Sommerhoff, *ibid.*, **39**, 76 (1906); Kremann, *ibid.*, **39**, 1022 (1906); Ciusa, *Gazz. chim. ital.*, **43**, II, 91 (1913); Ciusa and

with aniline is bright red; that with naphthalene, yellow. The compounds with amines are beautifully crystalline substances, procurable by warming the components together in alcohol, and are formed generally in the molecular proportions 1 to 1, although diphenylamine and quinoline form compounds in which two molecules of TNB are combined with one of the base.

Trinitrobenzene gives red colors with ammonia and with aqueous alkalies. On standing in the cold with methyl alcoholic sodium methylate, it yields 3,5-dinitroanisol by a metathetical reaction.[9]



On boiling with alcoholic soda solution it undergoes a partial reduction to form 3,3′,5,5′-tetranitroazoxybenzene.[10]



The first product, however, of the reaction of methyl alcoholic caustic alkali on TNB is a red crystalline addition product having the empirical composition $TNB \cdot CH_3ONa \cdot \frac{1}{2}H_2O$, isolated by Lobry de Bruyn and van Leent[11] in 1895. The structure of this substance has been discussed by Victor Meyer,[12] by Angeli,[13] by Meisenheimer,[14] and by Schlenck,[15] and is probably best represented by the formula which Meisenheimer suggested. It is thus

Vecchiotti, *Atti accad. Lincei,* 20, II, 377 (1911); 21, II, 161 (1912); Sastry, *J. Chem. Soc.,* 109, 270 (1916); Hammick and Sixsmith, *J. Chem. Soc.,* 972 (1939).

[9] Lobry de Bruyn, *Rec. trav. chim.,* 9, 208 (1890).

[10] Lobry de Bruyn and van Leent, *ibid.,* 13, 148 (1894).

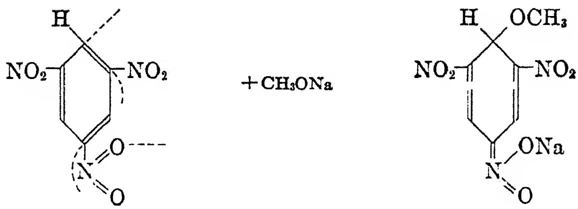
[11] *Ibid.,* 14, 150 (1895).

[12] *Ber.,* 29, 848 (1896).

[13] *Gazz. chim. ital.,* 27, II, 366 (1897). Compare also Hantzsch and Kissel, *Ber.,* 32, 3137 (1899).

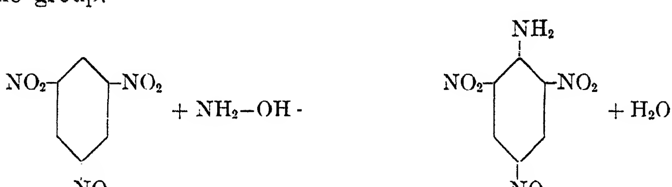
[14] *Ann.,* 323, 214, 241 (1902).

[15] *Ber.,* 47, 473 (1914).




probably the product of the 1,6-addition of sodium methylate to the conjugate system which runs through the ring and terminates in the oxygen of the nitro group. Busch and Kögel[16] have prepared di- and tri-alcoholates of TNB, and Giua[17] has isolated a compound of the empirical composition TNB·NaOH, to which he ascribed a structure similar to that indicated above. All these compounds when dry are dangerous primary explosives. They are soluble in water, and the solutions after acidification contain red, water-soluble acids which yield sparingly soluble salts with copper and other heavy metals, and the salts are primary explosives. The acids, evidently having the compositions TNB·$CH_3OH$, TNB·$H_2O$, etc., have not been isolated in a state of purity, and are reported to decompose spontaneously in small part into TNB, alcohol, water, etc., and in large part into oxalic acid, nitrous fumes, and colored amorphous materials which have not been identified. All the polynitro aromatic hydrocarbons react similarly with alkali, and the use of alkali in any industrial process for their purification is bad practice and extremely hazardous.

Trinitrobenzene reacts with hydroxylamine in cold alcohol solution, picramide being formed by the direct introduction of an amino group.[18]




Two or three nitro groups on the aromatic nucleus, particularly those in the 2,4-, 2,6-, and 2,4,6-positions, have a strong effect in increasing the chemical activity of the group or atom in the

[16] *Ber.*, **43**, 1549 (1910).

[17] *Gazz. chim. ital.*, **45**, II, 351 (1915).

[18] Meisenheimer and Patzig, *Ber.*, **39**, 2534 (1906).

1-position. Thus, the hydroxyl group of trinitrophenol is acidic, and the substance is called picric acid. A chlorine atom in the same position is like the chlorine of an acid chloride (picryl chloride), an amino group like the amino of an acid amide (trinitroaniline is picramide), and a methoxy like the methoxy of an ester (trinitroanisol has the reactions of methyl picrate). In general the picryl group affects the activity of the atom or group to which it is attached in the same way that the acyl or R—CO— group does. If the picryl group is attached to a carboxyl, the carboxyl will be expected to lose $CO_2$ readily, as pyruvic acid, $CH_3$—CO—COOH, does when it is heated with dilute sulfuric acid, and this indeed happens with the trinitrobenzoic acid from which TNB is commonly prepared. TNB itself will be expected to exhibit some of the properties of an aldehyde, of which the aldehydic hydrogen atom is readily oxidized to an acidic hydroxyl group, and it is in fact oxidized to picric acid by the action of potassium ferricyanide in mildly alkaline solution.[19] We shall see many examples of the same principle throughout the chemistry of the explosive aromatic nitro compounds.

Trinitrobenzene is less sensitive to impact than TNT, more powerful, and more brisant. The detonation of a shell or bomb, loaded with TNB, in the neighborhood of buildings or other construction which it is desired to destroy, creates a more damaging explosive wave than an explosion of TNT, and is more likely to cause the collapse of walls, etc., which the shell or bomb has failed to hit. Drop tests carried out with a 5-kilogram weight falling upon several decigrams of each of the various explosives contained in a small cup of iron (0.2 mm. thick), covered with a small iron disc of the same thickness, gave the following figures for the distances through which the weight must fall to cause explosion in 50 per cent of the trials.

| | CENTIMETERS |
|---|---|
| Trinitrobenzene | 150 |
| Trinitrotoluene | 110 |
| Hexanitrodiphenylamine ammonium salt | 75 |
| Picric acid | 65 |
| Tetryl | 50 |
| Hexanitrodiphenylamine | 45 |

[19] Hepp, *Ann.*, **215**, 344 (1882).

According to Dautriche,[20] the density of compressed pellets of TNB is as follows:

| Pressure: Kilos per Square Centimeter | Density |
|---|---|
| 275 | 1.343 |
| 685 | 1.523 |
| 1375 | 1.620 |
| 2060 | 1.641 |
| 2750 | 1.654 |
| 3435 | 1.662 |

The greatest velocity of detonation for TNB which Dautriche found, namely 7347 meters per second, occurred when a column of 10 pellets, 20 mm. in diameter and weighing 8 grams each, density 1.641 or 1.662, was exploded in a paper cartridge by means of an initiator of 0.5 gram of mercury fulminate and 80 grams of dynamite. The greatest which he found for TNT was 7140 meters per second, 10 similar pellets, density 1.60, in a paper cartridge exploded by means of a primer of 0.5 gram of fulminate and 25 grams of dynamite. The maximum value for picric acid was 7800 meters per second; a column of pellets of the same sort, density 1.71, exploded in a copper tube 20-22 mm. in diameter, by means of a primer of 0.5 gram of fulminate and 80 grams of dynamite. The highest velocity with picric acid in paper cartridges was 7645 meters per second with pellets of densities 1.73 and 1.74 and the same charge of initiator.

Velocity of detonation, other things being equal, depends upon the physical state of the explosive and upon the nature of the envelope which contains it. For each explosive there is an optimum density at which it shows its highest velocity of detonation. There is also for each explosive a minimum priming charge necessary to insure its complete detonation, and larger charges do not cause it to explode any faster. Figures for the velocity of detonation are of little interest unless the density is reported or unless the explosive is cast and is accordingly of a density which, though perhaps unknown, is easily reproducible. The cordeau of the following table[21] was loaded with TNT which was subsequently pulverized *in situ* during the drawing down of the lead tube:

[20] *Mém. poudres,* 16, 28 (1911-1912).

[21] Desvergnes, *Mém. poudres,* 19, 223 (1922).

| | Meters per Second |
|---|---|
| Cast trinitrobenzene | 7441 |
| Cast tetryl | 7229 |
| Cast trinitrotoluene | 7028 |
| Cast picric acid | 6777 |
| Compressed trinitrotoluene (*d.* 0.909) | 4961 |
| Compressed picric acid (*d.* 0.862) | 4835 |
| Cordeau | 6900 |

## Nitration of Chlorobenzene

The nitration of chlorobenzene is easier than the nitration of benzene and more difficult than the nitration of toluene. Trinitrochlorobenzene (picryl chloride) can be prepared on the plant scale by the nitration of dinitrochlorobenzene, but the process is expensive of acid and leads to but few valuable explosives which cannot be procured more cheaply and more simply from dinitrochlorobenzene by other processes. Indeed, there are only two important explosives, namely TNB and hexanitrobiphenyl, for the preparation of which picryl chloride could be used advantageously if it were available in large amounts. In the laboratory, picryl chloride is best prepared by the action of phosphorus pentachloride on picric acid.

During the early days of the first World War in Europe, electrolytic processes for the production of caustic soda were yielding in this country more chlorine than was needed by the chemical industries, and it was necessary to dispose of the excess. The pressure to produce toluene had made benzene cheap and abundant. The chlorine, which would otherwise have become a nuisance and a menace, was used for the chlorination of benzene. Chlorobenzene and dichlorobenzene became available, and dichlorobenzene since that time has been used extensively as an insecticide and moth exterminator. Dinitrodichlorobenzene was tried as an explosive under the name of *parazol.* When mixed with TNT in high-explosive shells, it did not detonate completely, but presented interesting possibilities because the unexploded portion, atomized in the air, was a vigorous itch-producer and lachrymator, and because the exploded portion yielded phosgene. The chlorine atom of chlorobenzene is unreactive, and catalytic processes[22] for replacing it by hydroxyl and amino groups had

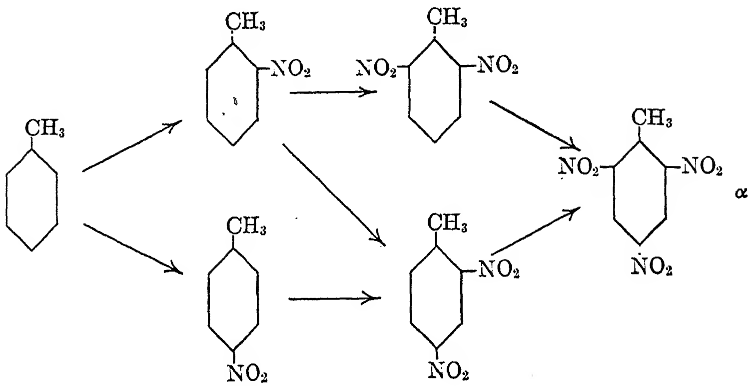
[22] Steam and silica gel to produce phenol from chlorobenzene, the Dow process with steam and a copper salt catalyst, etc.

not yet been developed. In dinitrochlorobenzene, however, the chlorine is active. The substance yields dinitrophenol readily by hydrolysis, dinitroaniline by reaction with ammonia, dinitromethylaniline more readily yet by reaction with methylamine. These and similar materials may be nitrated to explosives, and the third nitro group may be introduced on the nucleus much more readily, after the chlorine has been replaced by a more strongly *ortho-para* orienting group, than it may be before the chlorine has been so replaced. Dinitrochlorobenzene thus has a definite advantage over picryl chloride. It has the advantage also over phenol, aniline, etc. (from chlorobenzene by catalytic processes), that explosives can be made from it which cannot be made as simply or as economically from these materials. Tetryl and hexanitrodiphenylamine are examples. The possibilities of dinitrochlorobenzene in the explosives industry have not yet been fully exploited.

*Preparation of Dinitrochlorobenzene.* One hundred grams of chlorobenzene is added drop by drop to a mixture of 160 grams of nitric acid (*d.* 1.50) and 340 grams of sulfuric acid (*d.* 1.84) while the mixture is stirred mechanically. The temperature rises because of the heat of the reaction, but is not allowed to go above 50-55°. After all the chlorobenzene has been added, the temperature is raised slowly to 95° and is kept there for 2 hours longer while the stirring is continued. The upper layer of light yellow liquid solidifies when cold. It is removed, broken up under water, and rinsed. The spent acid, on dilution with water, precipitates an additional quantity of dinitrochlorobenzene. All the product is brought together, washed with cold water, then several times with hot water while it is melted, and finally once more with cold water under which it is crushed. Then it is drained and allowed to dry at ordinary temperature. The product, melting at about 50°, consists largely of 2,4-dinitrochlorobenzene, m.p. 53.4°, along with a small quantity of the 2,6-dinitro compound, m.p. 87-88°. The two substances are equally suitable for the manufacture of explosives. They yield the same trinitro compound, and the same final products by reaction with methylamine, aniline, etc., and subsequent nitration of the materials which are first formed. Dinitrochlorobenzene causes a severe itching of the skin, both by contact with the solid material and by exposure to its vapors.

**Trinitrotoluene** (TNT, trotyl, tolite, triton, tritol, trilite, etc.)

When toluene is nitrated, about 96 per cent of the material behaves in accordance with the rule of Crum Brown and Gibson.




In industrial practice the nitration is commonly carried out in three stages, the spent acid from the trinitration being used for the next dinitration, the spent acid from this being used for the mononitration, and the spent acid from this either being fortified

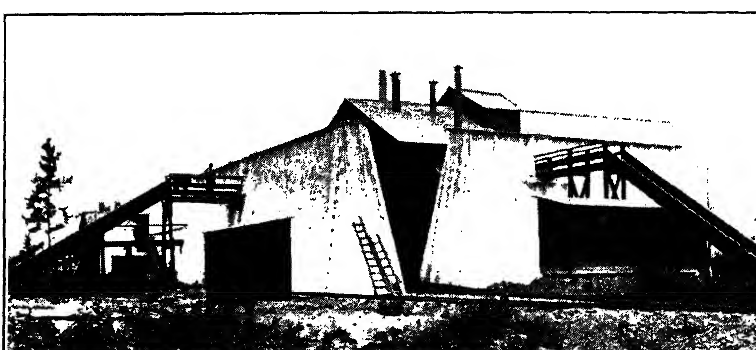
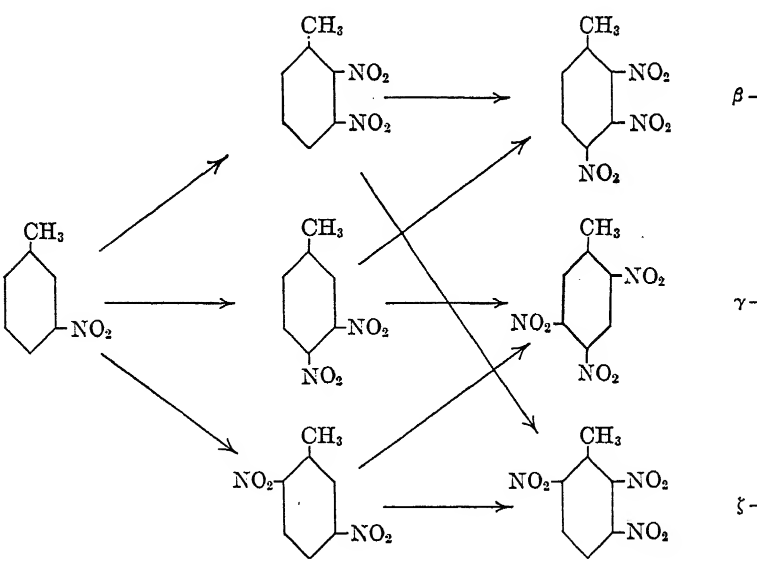


FIGURE 46. TNT Manufacturing Building, Showing Barricades and Safety Chutes. (Courtesy E. I. du Pont de Nemours and Company, Inc.)

for use again or going to the acid-recovery treatment. The principal products of the first stage are *o*- (b.p. 222.3°) and *p*-nitrotoluene (m.p. 51.9°) in relative amounts which vary somewhat according to the temperature at which the nitration is carried out. During the dinitration, the *para* compound yields only 2,4-dinitrotoluene (m.p. 70°), while the *ortho* yields the 2,4- and the 2,6- (m.p. 60.5°). Both these in the trinitration yield 2,4,6-trinitrotoluene or α-TNT. 2,4-Dinitrotoluene predominates in the product of the dinitration, and crude TNT generally contains a

small amount, perhaps 2 per cent, of this material which has escaped further nitration. The substance is stable and less reactive even than α-TNT, and a small amount of it in the purified TNT, if insufficient to lower the melting point materially, is not regarded as an especially undesirable impurity. The principal impurities arise from the *m*-nitrotoluene (b.p. 230-231°) which is formed to the extent of about 4 per cent in the product of the mononitration. We omit discussion of other impurities, such as the nitrated xylenes which might be present in consequence of impurities in the toluene which was used, except to point out that the same considerations apply to trinitro-*m*-xylene (TNX) as apply to 2,4-dinitrotoluene—a little does no real harm—while the nitro derivatives of *o*- and *p*-xylene are likely to form oils and are extremely undesirable. In *m*-nitrotoluene, the nitro group inhibits further substitution, the methyl group promotes it, the two groups disagree in respect to the positions which they activate, but substitution takes place under the orienting influence of the methyl group.




β-TNT or 2,3,4-trinitrotoluene (m.p. 112°) is the principal product of the nitration of *m*-nitrotoluene; γ-TNT or 2,4,5-trinitrotoluene (m.p. 104°) is present in smaller amount; and of ζ-TNT or 2,3,6-trinitrotoluene (m.p. 79.5°), the formation of

which is theoretically possible and is indicated above for that reason, there is not more than a trace.[23] During the trinitration a small amount of the α-TNT is oxidized to trinitrobenzoic acid, finally appearing in the finished product in the form of TNB, which, however, does no harm if it is present in small amount. At the same time some of the material is destructively oxidized and nitrated by the strong mixed acid to form tetranitromethane, which is driven off with the steam during the subsequent boiling and causes annoyance by its lachrymatory properties and unpleasant taste. The product of the trinitration is separated from the spent acid while still molten, washed with boiling water until free from acid, and grained—or, after less washing with hot water, subjected to purification by means of sodium sulfite.

In this country the crude TNT, separated from the wash water, is generally grained by running the liquid slowly onto the refrigerated surface of an iron vessel which surface is continually scraped by mechanical means. In France the material is allowed to cool slowly under water in broad and shallow wooden tubs, while it is stirred slowly with mechanically actuated wooden paddles. The cooling is slow, for the only loss of heat is by radiation. The French process yields larger and flatter crystals, flaky, often several millimeters in length. The crystallized crude TNT is of about the color of brown sugar and feels greasy to the touch. It consists of crystals of practically pure α-TNT coated with an oily (low-melting) mixture of β- and γ-TNT, 2,4-dinitrotoluene, and possibly TNB and TNX. It is suitable for many uses as an explosive, but not for high-explosive shells. The oily mixture of impurities segregates in the shell, and sooner or later exudes through the thread by which the fuze is attached. The exudate is disagreeable but not particularly dangerous. The difficulty is that exudation leaves cavities within the mass of the charge, perhaps a central cavity under the booster which may cause the shell to fail to explode. There is also the possibility that the shock of setback across a cavity in the rear of the charge may cause the shell to explode prematurely while it is still within the barrel of the gun.

The impurities may be largely removed from the crude TNT,

[23] 3,5-Dinitrotoluene, in which both nitro groups are *meta* to the methyl, is probably not formed during the dinitration, and δ- and ε-TNT, namely 3,4,5- and 2,3,5-trinitrotoluene, are not found among the final products of the nitration of toluene.

with a corresponding improvement in the melting point and appearance of the material, by washing the crystals with a solvent. On a plant scale, alcohol, benzene, solvent naphtha (mixed xylenes), carbon tetrachloride, and concentrated sulfuric acid have all been used. Among these, sulfuric acid removes dinitrotoluene most readily, and organic solvents the $\beta$- and $\gamma$-TNT,

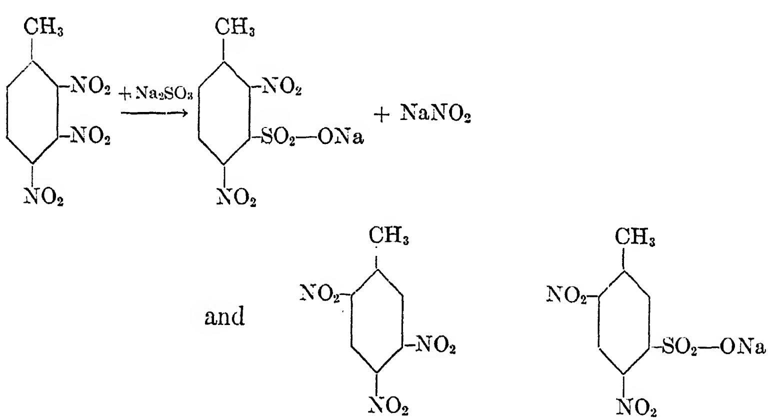
FIGURE 47. Commercial Sample of Purified TNT (25×).

but all of them dissolve away a portion of the $\alpha$-TNT with resulting loss. The material dissolved by the sulfuric acid is recovered by diluting with water. The organic solvents are recovered by distillation, and the residues, dark brown liquids known as "TNT oil," are used in the manufacture of non-freezing dynamite. The best process of purification is that in which the crude TNT is agitated with a warm solution of sodium sulfite. A 5 per cent solution is used, as much by weight of the solution as there is of the crude TNT. The sulfite leaves the $\alpha$-TNT (and any TNB, TNX, and 2,4-dinitrotoluene) unaffected, but reacts rapidly and completely with the $\beta$- and $\gamma$-TNT to form red-colored materials

which are readily soluble in water. After the reaction, the purified material is washed with water until the washings are colorless.

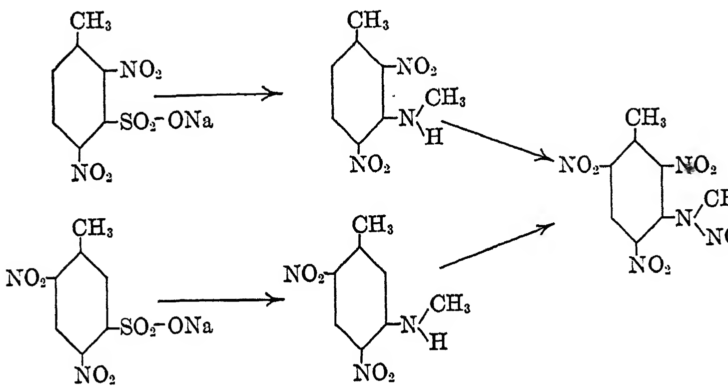
Muraour[24] believes the sulfite process for the purification of TNT to be an American invention. At any rate, the story of its discovery presents an interesting example of the consequences of working rightly with a wrong hypothesis. The nitro group in the *m*-position in β- and γ-TNT is *ortho*, or *ortho* and *para*, to two other nitro groups, and accordingly is active chemically. It is replaced by an amino group by the action of alcoholic ammonia both in the hot[25] and in the cold,[26] and undergoes similar reactions with hydrazine and with phenylhydrazine. It was hoped that it would be reduced more readily than the unactivated nitro groups of α- or symmetrical TNT, and that the reduction products could be washed away with warm water. Sodium polysulfide was tried and did indeed raise the melting point, but the treated material contained finely divided sulfur from which it could not easily be freed, and the polysulfide was judged to be unsuitable. In seeking for another reducing agent, the chemist bethought himself of sodium sulfite, which, however, does not act in this case as a reducing agent, and succeeded perfectly in removing the β- and γ-TNT.

The reaction consists in the replacement of the nitro by a sodium sulfonate group:



[24] *Bull. soc. chim.*, IV, **35**, 367 (1924); *Army Ordnance*, **5**, 507 (1924).
[25] Hepp, *Ann.*, **215**, 364 (1882).
[26] Giua, *Atti accad. Lincei*, **23**, II, 484 (1914); *Gazz. chim. ital.*, **45**, I, 345 (1915).

The soluble sulfonates in the deep red solution, if they are thrown into the sewer, represent a loss of about 4 per cent of all the toluene—a serious loss in time of war—as well as a loss of many pounds of nitro group nitrogen. The sulfonic acid group in these substances, like the nitro group which it replaced, is *ortho*, or *ortho* and *para*, to two nitro groups, and is active and still capable of undergoing the same reactions as the original nitro group. They may be converted into a useful explosive by reaction with methylamine and the subsequent nitration of the resulting dinitrotolylmethylamines, both of which yield 2,4,6-trinitrotolyl-3-methylnitramine or *m*-methyltetryl.

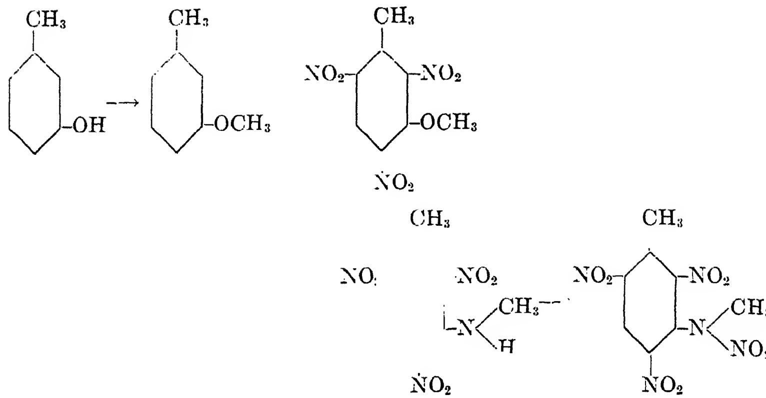


*m*-Methyltetryl, pale yellow, almost white, crystals from alcohol, m.p. 102°, was prepared in 1884 by van Romburgh[27] by the nitration of dimethyl-*m*-toluidine, and its structure was demonstrated fully in 1902 by Blanksma,[28] who prepared it by the synthesis indicated on the next page.

β- and γ-TNT lose their active nitro group by the action of aqueous alkali and yield salts of dinitro-*m*-cresol.[29] The mixed dinitro-*m*-cresols which result may be nitrated to trinitro-*m*-cresol, a valuable explosive. Their salts, like the picrates, are primary explosives and sources of danger. β- and γ-TNT react with lead oxide in alcohol to form lead dinitrocresolates, while α-TNT under the same conditions remains unaffected.

In plant-scale manufacture, TNT is generally prepared by a

[27] *Rec. trav. chim.*, 3, 414 (1884).
[28] *Ibid.*, 21, 327 (1902).
[29] Will, *Ber.*, 47, 711 (1914); Copisarow, *Chem. News*, 112, 283 (1915).



three-stage process, but processes involving one and two nitrations have also been used.

*Preparation of Trinitrotoluene* (Three Stages). A mixture of 294 grams of concentrated sulfuric acid (*d.* 1.84) and 147 grams of nitric acid (*d.* 1.42) is added slowly from a dropping funnel to 100 grams of toluene in a tall 600-cc. beaker, while the liquid is stirred vigorously with an electric stirrer and its temperature is maintained at 30° to 40° by running cold water in the vessel in which the beaker is standing. The addition of acid will require from an hour to an hour and a half. The stirring is then continued for half an hour longer without cooling; the mixture is allowed to stand over night in a separatory funnel; the lower layer of spent acid is drawn off; and the crude mononitrotoluene is weighed. One-half of it, corresponding to 50 grams of toluene, is taken for the dinitration.

The mononitrotoluene (MNT) is dissolved in 109 grams of concentrated sulfuric acid (*d.* 1.84) while the mixture is cooled in running water. The solution in a tall beaker is warmed to 50°, and a mixed acid, composed of 54.5 grams each of nitric acid (*d.* 1.50) and sulfuric acid (*d.* 1.84), is added slowly drop by drop from a dropping funnel while the mixture is stirred mechanically. The heat generated by the reaction raises the temperature, and the rate of addition of the acid is regulated so that the temperature of the mixture lies always between 90° and 100°. The addition of the acid will require about 1 hour. After the acid has been added, the mixture is stirred for 2 hours longer at 90-100° to complete the nitration. Two layers separate on standing. The upper layer consists largely of dinitrotoluene (DNT), but probably contains a certain amount of TNT. The trinitration in the laboratory is conveniently carried out without separating the DNT from the spent acid.

While the dinitration mixture is stirred actively at a temperature of about 90°, 145 grams of fuming sulfuric acid (*oleum* containing 15 per

cent free $SO_3$) is added slowly by pouring from a beaker. A mixed acid, composed of 72.5 grams each of nitric acid (*d.* 1.50) and 15 per cent oleum, is now added drop by drop with good agitation while the heat of the reaction maintains the temperature at 100-115°. After about three-quarters of the acid has been added, it will be found necessary to apply external heat to maintain the temperature. After all the acid has been added (during 1½ to 2 hours), the heating and stirring are continued for 2 hours longer at 100-115°. After the material has stood over night, the upper TNT layer will be found to have solidified to a hard cake, and the lower layer of spent acid to be filled with crystals. The acid is filtered through a Büchner funnel (without filter paper), and the cake is broken up and washed with water on the same filter to remove excess of acid. The spent acid contains considerable TNT in solution; this is precipitated by pouring the acid into a large volume of water, filtered off, rinsed with water, and added to the main batch. All the product is washed three or four times by agitating it vigorously with hot water under which it is melted. After the last washing, the TNT is granulated by allowing it to cool slowly under hot water while the stirring is continued. The product, filtered off and dried at ordinary temperature, is equal to a good commercial sample of crude TNT. It may be purified by dissolving in warm alcohol at 60° and allowing to cool slowly, or it may be purified by digesting with 5 times its weight of 5 per cent sodium hydrogen sulfite solution at 90° for half an hour with vigorous stirring, washing with hot water until the washings are colorless, and finally granulating as before. The product of this last treatment is equal to a good commercial sample of purified TNT. Pure $\alpha$-TNT, m.p. 80.8°, may be procured by recrystallizing this material once from nitric acid (*d.* 1.42) and once from alcohol.

Several of the molecular compounds of TNT with organic bases are listed below.[30] TNT and diphenylamine give an orange-brown color when warmed together or when moistened with alcohol, and the formation of a labile molecular compound of the two substances has been demonstrated.[31]

The compound of TNT with potassium methylate is a dark red powder which inflames or explodes when heated to 130-150°, and has been reported to explode spontaneously on standing at ordinary temperature. An aqueous solution of this compound, on the addition of copper tetrammine nitrate, gives a brick-red precipitate which, when dry, detonates violently at 120°. Pure TNT

[30] See references under TNB.
[31] Giua, *Gazz. chim. ital.*, 45, II, 357 (1915).

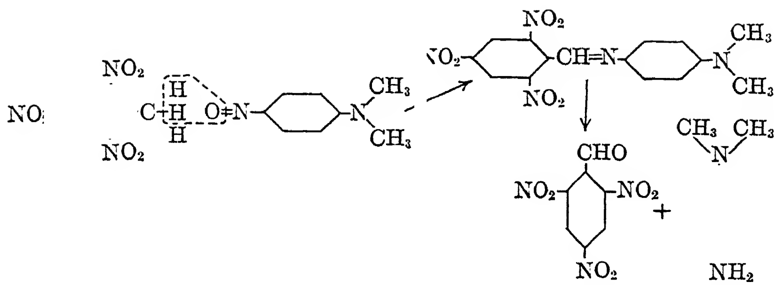
| Molecular Proportions | | M.P. | Description |
|---|---|---|---|
| TNT: | Substance | | |
| 1 | Aniline | 83–84° | Long brilliant red needles. |
| 1 | Dimethylaniline | | Violet needles. |
| 1 | *o*-Toluidine | 53–55° | Light red needles. |
| 1 | *m*-Toluidine | 62–63° | Light red needles. |
| 1 | α-Naphthylamine | 141.5° | Dark red needles. |
| 1 | β-Naphthylamine | 113.5° | Bright red prismatic needles. |
| 1 | β-Acetnaphthalide | 106° | Yellow needles. |
| 1 | Benzyl-β-naphthylamine | 106.5° | Brilliant crimson needles. |
| 1 | Dibenzyl-β-naphthylamine | 108° | Deep brick-red needles. |
| 1 | Benzaldehydephenylhydrazone | 84° | Dark red needles. |
| 1 | 2-Methylindole | 110° | Yellow needles. |
| 2 | Carbazole | 160° | Yellow needles. |
| 1 | Carbazole | 140–200° | Dark yellow needles. |

explodes or inflames when heated to about 230°, but Dupré[32] found that the addition of solid caustic potash to TNT at 160° caused immediate inflammation or explosion. A mixture of powdered solid caustic potash and powdered TNT inflames when heated, either slowly or rapidly, to 80°. A similar mixture with caustic soda inflames at 80° if heated rapidly, but may be heated to 200° without taking fire if the heating is slow. If a small fragment of solid caustic potash is added to melted TNT at 100°, it becomes coated with a layer of reaction product and nothing further happens. If a drop of alcohol, in which both TNT and KOH are soluble, is now added, the material inflames within a few seconds. Mixtures of TNT with potassium and sodium carbonate do not ignite when heated suddenly to 100°.

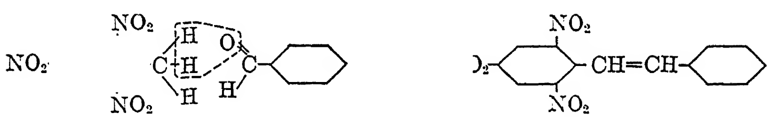
Since the methyl group of TNT is attached to a picryl group, we should expect it in some respects to resemble the methyl group of a ketone. Although acetone and other methyl ketones brominate with great ease, TNT does not brominate and may even be recrystallized from bromine. The methyl group of TNT, however, behaves like the methyl group of acetone in certain condensation reactions. In the presence of sodium carbonate TNT condenses with *p*-nitrosodimethylaniline to form the dimethylaminoanilide of trinitrobenzaldehyde,[33] from which trinitrobenzaldehyde and N,N-dimethyl-*p*-diaminobenzene are produced readily by acid hydrolysis.

[32] "Twenty-eighth Annual Report of H. M. Inspector of Explosives," 1903, p. 26.

[33] Sachs and Kempf, *Ber.*, **35**, 1222 (1902); Sachs and Everding, *ibid.*, **36**, 999 (1903).



If a drop of piperidine is added to a pasty mixture of TNT and benzaldehyde, the heat of the reaction is sufficient to cause the material to take fire. The same substances in alcohol or benzene solution condense smoothly in the presence of piperidine to form trinitrostilbene.[34]



*Preparation of Trinitrostilbene.* To 10 grams of TNT dissolved in 25 cc. of benzene in a 100-cc. round-bottom flask equipped with a reflux condenser, 6 cc. of benzaldehyde and 0.5 cc. of piperidine are added, and the mixture is refluxed on the water bath for half an hour. The material, while still hot, is poured into a beaker and allowed to cool and crystallize. The crystals, collected on a filter, are rinsed twice with alcohol and recrystallized from a mixture of 2 volumes of alcohol and 1 of benzene. Brilliant yellow glistening needles, m.p. 158°.

Trinitrotoluene, in addition to the usual reactions of a nitrated hydrocarbon with alkali to form dangerous explosive materials, has the property that its methyl group in the presence of alkali condenses with aldehydic substances in reactions which produce heat and which may cause fire. Aldehydic substances from the action of nitrating acid on wood are always present where TNT is being manufactured, and alkali of all kinds ought to be excluded rigorously from the premises.

Giua[35] reports that TNT may be distilled in vacuum without the slightest trace of decomposition. It boils at 210-212° at 10-20 mm. When heated for some time at 180-200°, or when exposed to

[34] Pfeiffer and Monath, *Ber.*, **39**, 1306 (1906); Ullmann and Geschwind, *ibid.*, **41**, 2296 (1908).

[35] Giua, "Chimica delle sostanze esplosive," Milan, 1919, p. 248.

sunlight[36] in open tubes, it undergoes a slow decomposition with a consequent lowering of the melting point. Exposure to sunlight in a vacuum in a sealed tube has much less effect. Verola[37] has found that TNT shows no perceptible decomposition at 150°, but that it evolves gas slowly and regularly at 180°. At ordinary temperatures, and even at the temperatures of the tropics, it is stable in light-proof and air-tight containers—as are in general all the aromatic nitro explosives—and it does not require the same surveillance in storage that nitrocellulose and smokeless powder do.

The solubility[38] of trinitrotoluene in various solvents is tabulated below.

SOLUBILITY OF TRINITROTOLUENE

(Grams per 100 grams of solvent)

| Temp. | Water | $CCl_4$ | Benzene | Toluene | Acetone | 95% Alcohol | $CHCl_3$ | Ether |
|---|---|---|---|---|---|---|---|---|
| 0° | 0.0100 | 0.20 | 13 | 28 | 57 | 0.65 | 6 | 1.73 |
| 5° | 0.0105 | 0.25 | 24 | 32 | 66 | 0.75 | 8.5 | 2.08 |
| 10° | 0.0110 | 0.40 | 36 | 38 | 78 | 0.85 | 11 | 2.45 |
| 15° | 0.0120 | 0.50 | 50 | 45 | 92 | 1.07 | 15 | 2.85 |
| 20° | 0.0130 | 0.65 | 67 | 55 | 109 | 1.23 | 19 | 3.29 |
| 25° | 0.0150 | 0.82 | 88 | 67 | 132 | 1.48 | 25 | 3.80 |
| 30° | 0.0175 | 1.01 | 113 | 84 | 156 | 1.80 | 32.5 | 4.56 |
| 35° | 0.0225 | 1.32 | 144 | 104 | 187 | 2.27 | 45 | ... |
| 40° | 0.0285 | 1.75 | 180 | 130 | 228 | 2.92 | 66 | ... |
| 45° | 0.0360 | 2.37 | 225 | 163 | 279 | 3.70 | 101 | ... |
| 50° | 0.0475 | 3.23 | 284 | 208 | 346 | 4.61 | 150 | ... |
| 55° | 0.0570 | 4.55 | 361 | 272 | 449 | 6.08 | 218 | ... |
| 60° | 0.0675 | 6.90 | 478 | 367 | 600 | 8.30 | 302 | ... |
| 65° | 0.0775 | 11.40 | 665 | 525 | 843 | 11.40 | 442 | ... |
| 70° | 0.0875 | 17.35 | 1024 | 826 | 1350 | 15.15 | ... | ... |
| 75° | 0.0975 | 24.35 | 2028 | 1685 | 2678 | 19.50 | ... | ... |
| 80° | 0.1075 | ... | ... | ... | ... | ... | ... | ... |
| 85° | 0.1175 | ... | ... | ... | ... | ... | ... | ... |
| 90° | 0.1275 | ... | ... | ... | ... | ... | ... | ... |
| 95° | 0.1375 | ... | ... | ... | ... | ... | ... | ... |
| 100° | 0.1475 | ... | ... | ... | ... | ... | ... | ... |

[36] Molinari and Quartieri, "Notizie sugli esplodenti in Italia," Milan, 1913, p. 157.

[37] *Mém. poudres,* 16, 40 (1911-1912).

[38] Taylor and Rinkenbach, *J. Am. Chem. Soc.,* 45, 44 (1923).

Dautriche found the density of powdered and compressed TNT to be as follows:

| Pressure: Kilos per Square Centimeter | Density |
|---|---|
| 275 | 1.320 |
| 685 | 1.456 |
| 1375 | 1.558 |
| 2060 | 1.584 |
| 2750 | 1.599 |
| 3435 | 1.602 |
| 4125 | 1.610 |

Trinitrotoluene was prepared by Wilbrand[39] in 1863 by the nitration of toluene with mixed acid, and in 1870 by Beilstein and Kuhlberg[40] by the nitration of *o*- and *p*-nitrotoluene, and by Tiemann[41] by the nitration of 2,4-dinitrotoluene. In 1891 Haussermann[42] with the Griesheim Chem. Fabrik undertook its manufacture on an industrial scale. After 1901 its use as a military explosive soon became general among the great nations. In the first World War all of them were using it.

## Trinitroxylene (TNX)

In *m*-xylene the two methyl groups agree in activating the same positions, and this is the only one of the three isomeric xylenes which can be nitrated satisfactorily to yield a trinitro derivative. Since the three isomers occur in the same fraction of coal tar and cannot readily be separated by distillation, it is necessary to separate them by chemical means. When the mixed xylenes are treated with about their own weight of 93 per cent sulfuric acid for 5 hours at 50°, the *o*-xylene (b.p. 144°) and the *m*-xylene (b.p. 138.8°) are converted into water-soluble sulfonic acids, while the *p*-xylene (b.p. 138.5°) is unaffected. The aqueous phase is removed, diluted with water to about 52 per cent acidity calculated as sulfuric acid, and then heated in an autoclave at 130° for 4 hours. The *m*-xylene sulfonic acid is converted to *m*-xylene, which is removed. The *o*-xylene sulfonic acid, which remains in solution, may be converted into *o*-xylene by autoclaving at a higher temperature. The nitration of *m*-xylene is conveniently carried out in three steps. The effect of the two methyl

[39] *Ann.*, 128, 178 (1863).
[40] *Ber.*, 3, 202 (1870).
[41] *Ber.*, 3, 217 (1870).
[42] *Z. angew. Chem.*, 1891, p. 508; *J. Soc. Chem. Ind.*, 1891, p. 1028.

groups is so considerable that the introduction of the third nitro group may be accomplished without the use of fuming sulfuric acid. Pure TNX, large almost colorless needles from benzene, melts at 182.3°.

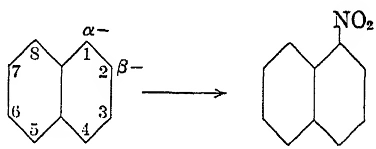
Trinitroxylene is not powerful enough for use alone as a high explosive, and it does not always communicate an initial detonation throughout its mass. It is used in commercial dynamites, for which purpose it does not require to be purified and may contain an oily mixture of isomers and other nitrated xylenes. Its large excess of carbon suggests that it may be used advantageously in conjunction with an oxidizing agent. A mixture of 23 parts of TNX and 77 parts of ammonium nitrate, ground intimately together in a black powder mill, has been used in high-explosive shells. It was loaded by compression. Mixtures, about half and half, of TNX with TNT and with picric acid are semi-solid when warm and can be loaded by pouring. The eutectic of TNX and TNT contains between 6 and 7 per cent of TNX and freezes at 73.5°. It is substantially as good an explosive as TNT. A mixture of 10 parts TNX, 40 parts TNT, and 50 parts picric acid can be melted readily under water. In explosives such as these the TNX helps by lowering the melting point, but it also attenuates the power of the more powerful high explosives with which it is mixed. On the other hand, these mixtures take advantage of the explosive power of TNX, such as that power is, and are themselves sufficiently powerful and satisfactory for many purposes—while making use of a raw material, namely *m*-xylene, which is not otherwise applicable for use in the manufacture of military explosives.

## Nitro Derivatives of Naphthalene

Naphthalene nitrates more readily than benzene, the first nitro group taking the α-position which is *ortho* on one nucleus to the side chain which the other nucleus constitutes. The second nitro group takes one or another of the expected positions, either the position *meta* to the nitro group already present or one of the α-positions of the unsubstituted nucleus. The dinitration of naphthalene in actual practice thus produces a mixture which consists almost entirely of three isomers. Ten different isomeric dinitronaphthalenes are possible, seven of which are derived from α-nitronaphthalene, seven from β-nitronaphthalene, and four

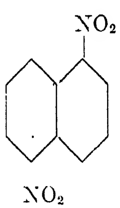
from both the α- and the β-compounds. After two nitro groups have been introduced, conflicts of orienting tendencies arise and polynitro compounds are formed, among others, in which nitro groups occur *ortho* and *para* to one another. Only four nitro groups can be introduced into naphthalene by direct nitration.

The mononitration of naphthalene takes place easily with a mixed acid which contains only a slight excess of one equivalent of $HNO_3$.

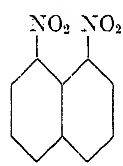


For the di-, tri-, and tetranitrations increasingly stronger acids and higher temperatures are necessary. In the tetranitration oleum is commonly used and the reaction is carried out at 130°.

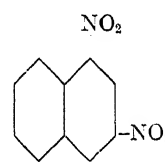
The nitration of α-nitronaphthalene[43] (m.p. 59-60°) yields a mixture of α- or 1,5-dinitronaphthalene (silky needles, m.p. 216°), β- or 1,8-dinitronaphthalene (rhombic leaflets, m.p. 170-172°), and γ- or 1,3-dinitronaphthalene (m.p. 144-145°).



α-



β-



γ-

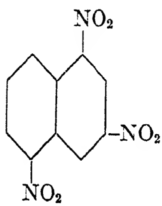
The commercial product of the dinitration melts at about 140°, and consists principally of the α- and β-compounds. The nitration of naphthalene at very low temperatures,[44] −50° to −60°, gives good yields of the γ- compound, and some of this material is undoubtedly present in the ordinary product.

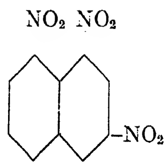
The nitration of α-dinitronaphthalene yields α- or 1,3,5-trinitronaphthalene (monoclinic crystals, m.p. 123°), γ- or 1,4,5-

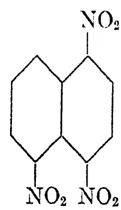
[43] Roussin, *Comp. rend.*, **52**, 796 (1861); Darmstädter and Wickelhaus, *Ann.*, **152**, 301 (1869); Aguiar, *Ber.*, **2**, 220 (1869); **3**, 29 (1870); **5**, 370 (1872); Beilstein and Kuhlberg, *Ann.*, **169**, 86 (1873); Beilstein and Kurbatow, *Ber.*, **13**, 353 (1880); *Ann.*, **202**, 219, 224 (1880); Julius, *Chem. Ztg.*, **18**, 180 (1894); Gassmann, *Ber.*, **29**, 1243, 1521 (1896); Friedländer, *ibid.*, **32**, 3531 (1899).

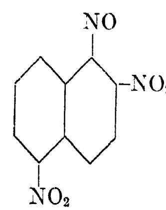
[44] Pictet, *Comp. rend.*, **116**, 815 (1893).

trinitronaphthalene (glistening plates, m.p. 147°), and δ- or 1,2,5-trinitronaphthalene (m.p. 112-113°). The nitration of β-dinitronaphthalene yields β- or 1,3,8-trinitronaphthalene (monoclinic crystals, m.p. 218°), and the same substance, along with some α-trinitronaphthalene, is formed by the nitration of γ-dinitronaphthalene.


α-

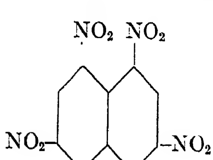


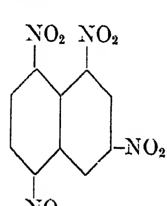

γ-

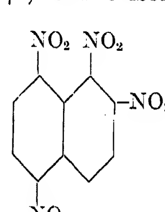

δ-

All these isomers occur in commercial trinitronaphthalene, known as *naphtite*, which melts at about 110°.

The nitration of α-, β-, and γ-trinitronaphthalene yields γ- or 1,3,5,8-tetranitronaphthalene (glistening tetrahedrons, m.p. 194-195°). The nitration of the β-compound also yields β- or 1,3,6,8-tetranitronaphthalene (m.p. 203°), and that of the δ-trinitro compound yields δ- or 1,2,5,8-tetranitronaphthalene (glistening prisms which decompose at 270° without melting), a substance which may be formed also by the introduction of a fourth nitro group into γ-trinitronaphthalene. The nitration of 1,5-dinitronaphthalene[45] yields α-tetranitronaphthalene (rhombic crystals, m.p. 259°) (perhaps 1,3,5,7-tetranitronaphthalene), and this substance is also present in the crude product of the tetranitration, which, however, consists largely of the β-, γ-, and δ-isomers.




γ-


δ-

The crude product is impure and irregular in its appearance; it is commonly purified by recrystallization from glacial acetic acid.

[45] Aguiar, *Ber.*, 5, 374 (1872).

The purified material consists of fine needle crystals which melt at about 220° and have the clean appearance of a pure substance but actually consist of a mixture of isomers.

None of the nitrated naphthalenes is very sensitive to shock. α-Nitronaphthalene is not an explosive at all and cannot be detonated. Dinitronaphthalene begins to show a feeble capacity for explosion, and trinitronaphthalene stands between dinitrobenzene and dinitrotoluene in its explosive power. Tetranitronaphthalene is about as powerful as TNT, and distinctly less sensitive to impact than that explosive. Vennin and Chesneau report that the nitrated naphthalenes, charged in a manometric bomb at a density of loading of 0.3, gave on firing the pressures indicated below.[46]

| | Kilos per Square Centimeter |
|---|---|
| Mononitronaphthalene..... | 1208 |
| Dinitronaphthalene........ | 2355 |
| Trinitronaphthalene........ | 3275 |
| Tetranitronaphthalene ..... | 3745 |

The nitrated naphthalenes are used in dynamites and safety explosives, in the Favier powders, *grisounites*, and *naphtalites* of France, in the *cheddites* which contain chlorate, and for military purposes to some extent in mixtures with ammonium nitrate or with other aromatic nitro compounds. Street,[47] who proposed their use in cheddites, also suggested a fused mixture of mononitronaphthalene and picric acid for use as a high explosive. *Schneiderite*, used by France and by Italy and Russia in shells during the first World War, consisted of 1 part dinitronaphthalene and 7 parts ammonium nitrate, intimately incorporated together by grinding in a black powder mill, and loaded by compression. A mixture (MMN) of 3 parts mononitronaphthalene and 7 parts picric acid, fused together under water, was used in drop bombs and was insensitive to the impact of a rifle bullet. A mixture (MDN) of 1 part dinitronaphthalene and 4 parts picric acid melts at about 105-110°; it is more powerful than the preceding and is also less sensitive to shock than picric acid alone. The

[46] Vennin and Chesneau, "Les poudres et explosifs et les mesures de sécurité dans les mines de houille," Paris and Liége, 1914, p. 269.

[47] *Mon. Sci.*, 1898, p. 495.

Germans used a mine explosive consisting of 56 per cent potassium perchlorate, 32 per cent dinitrobenzene, and 12 per cent dinitronaphthalene.[48] Their *Tri-Trinal* for small-caliber shells was a compressed mixture of 2 parts of TNT (*Tri*) with 1 of trinitronaphthalene (*Trinal*), and was used with a booster of compressed picric acid.

Trinitronaphthalene appears to be a genuine stabilizer for nitrocellulose, a true inhibitor of its spontaneous decomposition. Marqueyrol found that a nitrocellulose powder containing 10 per cent of trinitronaphthalene is as stable as one which contains 2 per cent of diphenylamine. The trinitronaphthalene has the further effect of reducing both the hygroscopicity and the temperature of combustion of the powder.

## Hexanitrobiphenyl

2,2',4,4',6,6'-Hexanitrobiphenyl was first prepared by Ullmann and Bielecki[49] by boiling picryl chloride in nitrobenzene solution with copper powder for a short time. The solvent is necessary in order to moderate the reaction, for picryl chloride and copper powder explode when heated alone to about 127°. Ullmann and Bielecki also secured good yields of hexanitrobiphenyl by working in toluene solution, but found that a small quantity of trinitrobenzene was formed (evidently in consequence of the presence of moisture). Hexanitrobiphenyl crystallizes from toluene in light-yellow thick crystals which contain ½ molecule of toluene of crystallization. It is insoluble in water, and slightly soluble in alcohol, acetone, benzene, and toluene, m.p. 263°. It gives a yellow color with concentrated sulfuric acid, and a red with alcohol to which a drop of ammonia water or aqueous caustic soda has been added. It is neutral, of course, and chemically unreactive toward metals, and is reported to be non-poisonous.

Hexanitrobiphenyl cannot[50] be prepared by the direct nitration

[48] Naoum, "Schiess- und Sprengstoffe," Dresden and Leipzig, 1927, p. 62.

[49] *Ber.*, 34, 2174 (1901).

[50] The effect may be steric, although there is evidence that the dinitrophenyl group has peculiar orienting and resonance effects. Rinkenbach and Aaronson, *J. Am. Chem. Soc.*, 52, 5040 (1930), report that *sym*-diphenylethane yields only very small amounts of hexanitrodiphenylethane under the most favorable conditions of nitration.

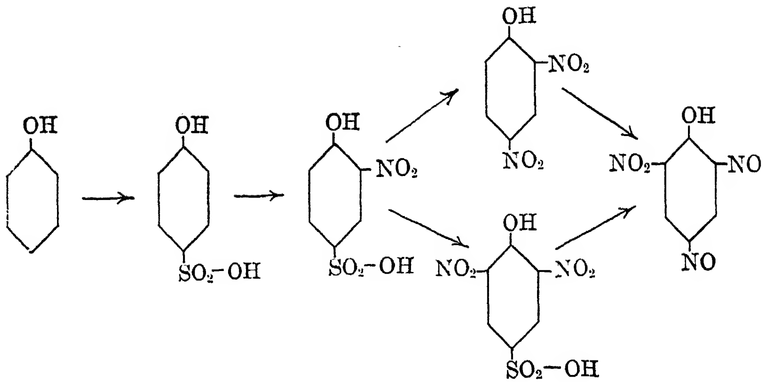
of biphenyl. The most vigorous nitration of that hydrocarbon yields only 2,2′,4,4′-tetranitrobiphenyl, yellowish prisms from benzene, m.p. 163°.

Jahn in a patent granted in 1918[51] states that hexanitrobiphenyl is about 10 per cent superior to hexanitrodiphenylamine. Fifty grams in the lead block produced a cavity of 1810 cc., while the same weight of hexanitrodiphenylamine produced one of 1630 cc. Under a pressure of 2500 atmospheres, it compresses to a density of about 1.61.

**Picric Acid** (melinite, lyddite, pertite, shimose, etc.)

The *ortho-para* orienting hydroxyl group of phenol promotes nitration greatly and has the further effect that it "weakens" the ring and makes it more susceptible to oxidation. Nitric acid attacks phenol violently, oxidizing a portion of it to oxalic acid, and produces resinous by-products in addition to a certain amount of the expected nitro compounds. The carefully controlled action of mixed acid on phenol gives a mixture of *o*-nitrophenol (yellow crystals, m.p. 45°, volatile with steam) and *p*-nitrophenol (white crystals, m.p. 114°, not volatile with steam), but the yields are not very good. When these mononitrophenols are once formed, their nitro groups "activate" the same positions as the hydroxyls do, but the nitro groups also inhibit substitution, and their further nitration may now be carried out more smoothly. *p*-Nitrophenol yields 2,4-dinitrophenol (m.p. 114-115°), and later picric acid. *o*-Nitrophenol yields 2,4- and 2,6-dinitrophenol (m.p. 63-64°), both of which may be nitrated to picric acid, but the nitration of *o*-nitrophenol is invariably accompanied by losses resulting from its volatility. The straightforward nitration of phenol cannot be carried out successfully and with satisfying yields. In practice the phenol is sulfonated first, and the sulfonic acid is then nitrated. The use of sulfuric acid (for the sulfonation) in this process amounts to its use as an inhibitor or moderator of the nitration, for the *meta* orienting sulfonic acid group at first slows down the introduction of nitro groups until it is itself finally replaced by one of them.

[51] U. S. Pat. 1,253,691 (1918).




The sulfonation of phenol at low temperatures produces the *o*-sulfonic acid, and at high temperatures the *p*-sulfonic acid along with more or less of the di- and even of the trisulfonic acids according to the conditions of the reaction. All these substances yield picric acid as the final product of the nitration.[52]

Unless carefully regulated the production of picric acid from phenol is accompanied by losses, either from oxidation of the material with the production of red fumes which represent a loss of fixed nitrogen or from over sulfonation and the loss of unconverted water-soluble nitrated sulfonic acids in the mother liquors. Olsen and Goldstein[53] have described a process which yields 220 parts of picric acid from 100 parts of phenol. In France, where dinitrophenol was used during the first World War in mixtures with picric acid which were loaded by pouring, Marqueyrol and his associates[54] have worked out the details of a four-stage process from the third stage of which dinitrophenol may be removed if it is desired. The steps are: (1) sulfonation; (2) nitration to the water-soluble mononitrosulfonic acid; (3) nitration to dinitrophenol, which is insoluble in the mixture and separates out, and to the dinitrosulfonic acid which remains in solution; and (4) further nitration to convert either the soluble material or both of the substances to picric acid. The process is economical of acid and gives practically no red fumes, but the reported yields are inferior to those reported by Olsen and Goldstein. The

[52] Cf. King, *J. Chem. Soc.*, **119**, 2105 (1921).

[53] Olsen and Goldstein, *Ind. Eng. Chem.*, **16**, 66 (1924).

[54] Marqueyrol and Loriette, *Bull. soc. chim.*, **25**, 376 (1919); Marqueyrol and Carré, *ibid.*, **27**, 195 (1920).

dinitrophenol as removed contains some picric acid, but this is of no disadvantage because the material is to be mixed with picric acid anyway for use as an explosive.

*Preparation of Picric Acid* (Standard Method). Twenty-five grams of phenol and 25 grams of concentrated sulfuric acid (*d.* 1.84) in a round-

FIGURE 48. Commercial Sample of Picric Acid (25×).

bottom flask equipped with an air condenser are heated together for 6 hours in an oil bath at 120°. After the material has cooled, it is diluted with 75 grams of 72 per cent sulfuric acid (*d.* 1.64). To the resulting solution, in an Erlenmeyer flask in the hood, 175 cc. of 70 per cent nitric acid (*d.* 1.42) is added slowly, a drop at a time, from a dropping funnel. When all the nitric acid has been added and the vigorous reaction has subsided, the mixture is heated for 2 hours on the steam bath to complete the nitration. The next morning the picric acid will be found to have separated in crystals. These are transferred to a porcelain filter, washed with small portions of water until the washings are free from sulfate, and dried in the air. The crude product, which is equal in quality to a good commercial sample, is purified by boiling it

with water, in the proportion of 15 grams to the liter, filtering hot, and allowing to cool slowly. The heavy droplets of brown oil which dissolve only slowly during this boiling ought to be discarded. Pure picric acid crystallizes from water in pale yellow flat needles, m.p. 122.5°. It may be obtained in crystals which are almost white by recrystallizing from aqueous hydrochloric acid.

The best process for the production of dinitrophenol is probably the autoclaving of dinitrochlorobenzene with aqueous caustic soda. The product is obtained on acidification and is used as such, or is nitrated to picric acid for the commercial production of that material by the so-called synthetic process.

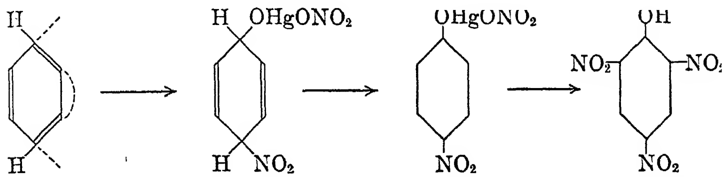
The "catalytic process" for the production of picric acid directly from benzene in one step by the action of nitric acid in the presence of mercuric nitrate has much theoretical interest and has been applied, though not extensively, in plant-scale manufacture. It yields about as much picric acid as is procurable from the same weight of benzene by the roundabout method of sulfonating the benzene, converting the benzene sulfonic acid into phenol, and nitrating the phenol to picric acid—and the benzene which is not converted to picric acid is for the most part recovered as such or as nitrobenzene. The first mention of the process appears to be in the patent of Wolffenstein and Boeters.[55]

*Preparation of Picric Acid* (Catalytic Process). Two hundred grams of benzene in a 2-liter round-bottom flask equipped with a sealed-on condenser is refluxed on the sand bath for 7 hours with 600 cc. of nitric acid (*d.* 1.42) in which 10 grams of mercuric nitrate has been dissolved. The material is then transferred to another flask and distilled with steam. Benzene comes over, then nitrobenzene, then finally and slowly a mixture of dinitrobenzene and dinitrophenol. The distillation is continued until all volatile matter has been removed. The liquid in the flask is filtered hot and allowed to crystallize. If the picric acid is not sufficiently pure, it is recrystallized from hot water.

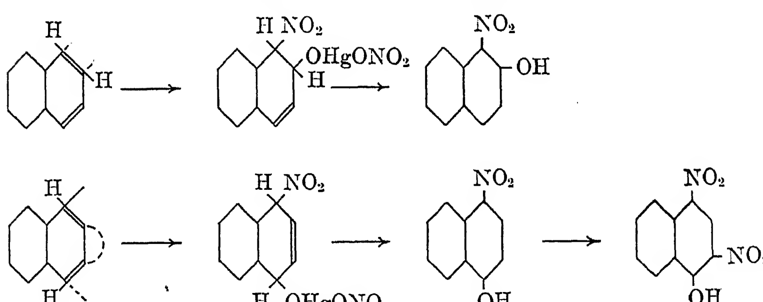
Mercuric nitrate combines with benzene to form a deep-brown or black addition compound, the probable structure of which is indicated below. This material when warmed with nitric acid is oxidized with the production of red fumes and the formation of

[55] Wolffenstein and Boeters, Ger. Pat. 194,883 (1908); Ger. Pat. 214,045 (1909); Ramy, Brit. Pat. 125,461 (1918); MacDonald and Calvert, Brit. Pats. 126,062, 126,084, 126,675, 126,676 (1918); Brewster, Brit. Pat. 131,403 (1919).

a yellow nitrophenolate of mercuric nitrate. By the continued action of the acid this is nitrated to the trinitrophenolate and decomposed with the formation of picric acid and the regeneration of mercuric nitrate.[56]



The addition of mercuric nitrate is here written as a 1,4-addition, but 1,2-addition would give the same final product, and there is no evidence in the facts concerning benzene which enables us to choose between the alternative hypotheses. Toluene yields trinitro-*m*-cresol by a similar series of reactions, and it is clear that the nitro group in the addition product of mercuric nitrate and toluene has taken either the 2-, the 4-, or the 6-position, that is, one or the other of the positions activated by the methyl group. In the addition of mercuric nitrate to naphthalene, the nitro group correspondingly may be supposed to go to the active α-position. If the addition is 1,2-, the product on oxidation will yield a derivative of β-naphthol. If it is 1,4-, it will yield a derivative of α-naphthol. The two possibilities are indicated below.



Gentle treatment of naphthalene with nitric acid containing mercuric nitrate yields, 2,4-dinitro-α-naphthol in conformity with the belief that the first addition product is 1,4- as represented by the second of the above formulations.

Picric acid was obtained in 1771 by Woulff, who found that

[56] Davis, Worrall, Drake, Helmkamp, and Young, *J. Am. Chem. Soc.*, **43**, 594 (1921); Davis, *ibid.*, **44**, 1588 (1922). Davis, U. S. Pat. 1,417,368 (1922).

the action of nitric acid on indigo yielded a material which dyed silk yellow. Hausmann[57] isolated the substance in 1778, and reported further studies upon it in 1788, noting particularly its bitter taste. Welter[58] in 1799 obtained picric acid by the action of nitric acid on silk, and the material came to be known generally as "Welter's bitter." Its preparation from indigo, aloes, resin, and other organic substances was studied by many chemists, among them Fourcroy and Vauquelin, Chevreul, Liebig, Wöhler, Robiquet, Piria, Delalande, and Stenhouse. Its preparation from oil of eucalyptus was suggested during the first World War. It was given the name of *acide picrique* by Dumas; *cf.* Greek πικρός = bitter, old English *puckery*. Its relation to phenol was demonstrated in 1841 by Laurent,[59] who prepared it by the nitration of that substance, and its structure was proved fully by Hepp,[60] who procured it by the oxidation of *sym*-trinitrobenzene.

Picric acid is a strong acid; it decomposes carbonates and may be titrated with bases by the use of sodium alizarine sulfonate as an indicator. It is a fast yellow dye for silk and wool. It attacks the common metals, except aluminum and tin, and produces dangerously explosive salts. *Cordeau Lheure*, which was long used extensively in France, was made by filling a tin pipe with fused picric acid and later drawing down to the desired diameter. It had the disadvantage that the metal suffered from the "tin disease," became unduly brittle, and changed to its gray allotropic modification. Picric acid and nitrophenols, when used in ammunition, are not allowed to come in contact with the metal parts. Shells which are to be loaded with these explosives are first plated on the inside with tin or painted with asphaltum varnish or Bakelite.

Dupré[61] in 1901 reported experiments which indicated that the picrates of calcium, lead, and zinc, formed *in situ* from melted picric acid are capable of initiating the explosion of that material. Kast[62] found that the dehydrated picrates are more sensitive than those which contain water of crystallization. The data tabulated

[57] *J. Phys.* 32, 165 (1788).
[58] *Ann. chim. phys.*, I, 29, 301 (1799).
[59] *Ann. chim. phys.*, III, 3, 221 (1841).
[60] Hepp, *loc. cit.*
[61] *Mém. poudres*, 11, 92 (1901).
[62] *Z. ges. Schiess- u. Sprengstoffw.*, 6, 7, 31, 67 (1911). See also Will, *ibid.*, 1, 209 (1906); Silberrad and Phillips, *J. Chem. Soc.*, 93, 474 (1908).

below have been published recently by J. D. Hopper.[63] Explosion temperature was determined as the temperature necessary to cause ignition or explosion in exactly 5 seconds when a thin-walled copper shell containing a few milligrams of the explosive was dipped into a molten metal bath to a constant depth. The minimum drop test was taken as the least distance through which a 2-kilogram weight must fall, in a standard apparatus,[64] to produce detonation or ignition in one or more instances among ten trials.

| Substance | Degree of Hydration | Temperature of Drying, °C. | Minimum Drop Test 2-kilo Weight, Inches | Explosion Temperature, °C. |
|---|---|---|---|---|
| Mercury fulminate | Anhydrous | ... | 2 | 210 |
| Tetryl | Anhydrous | ... | 8 | 260 |
| TNT | Anhydrous | ... | 14 | 470 |
| Picric acid | Anhydrous | ... | 14 | 320 |
| Ammonium picrate | Anhydrous | ... | 17 | 320 |
| Sodium picrate | 1 $H_2O$ | 50 | 17 | 360 |
| Sodium picrate | Anhydrous | 150 | 15 | ... |
| Sodium dinitrophenolate | 1 $H_2O$ | 100 | 16 | 370 |
| Sodium dinitrophenolate | Anhydrous | 150 | 15 | ... |
| Copper picrate | 3 $H_2O$ | 25 | 19 | 300 |
| Copper picrate | Anhydrous | 150 | 12 | ... |
| Zinc picrate | 6 $H_2O$ | 25 | 34 | 310 |
| Zinc picrate | Anhydrous | 150 | 12 | ... |
| Cadmium picrate | 8 $H_2O$ | 25 | 35 | 340 |
| Cadmium picrate | Anhydrous | 150 | 12 | ... |
| Nickel picrate | 6 $H_2O$ | 25 | 26 | 390 |
| Nickel picrate | .... | 100 | 9 | ... |
| Nickel picrate | Anhydrous | 150 | 4 | ... |
| Aluminum picrate | 10 $H_2O$ | 25 | 36 | 360 |
| Aluminum picrate | 2 $H_2O$ | 80 | 16 | ... |
| Aluminum picrate | .... | 100 | 16 | ... |
| Chromium picrate | 13 $H_2O$ | 25 | 36 | 330 |
| Chromium picrate | .... | 80 | 10 | ... |
| Chromium picrate | 1 $H_2O$ | 100 | 8 | ... |
| Ferrous picrate | 8 $H_2O$ | 25 | 36 | 310 |
| Ferrous picrate | .... | 100 | 14 | ... |
| Ferric picrate | $x$ $H_2O$ | 25 | 36 | 295 |
| Ferric picrate | .... | 80 | | |
| Ferric picrate | .... | 100 | | |
| Ferric picrate | .... | 150 | | |

[63] *J. Franklin Inst.*, 225, 219 (1938).
[64] H. S. Deck, *Army Ordnance*, 7, 34 (1926).

Cast picric acid has a density of about 1.64. The density of pellets of compressed picric acid, according to Dautriche, is as follows.

| Pressure: Kilos per Square Centimeter | Density |
|---|---|
| 275 | 1.315 |
| 685 | 1.480 |
| 1375 | 1.614 |
| 2060 | 1.672 |
| 2750 | 1.714 |
| 3435 | 1.731 |
| 4125 | 1.740 |

The use of picric acid as an explosive appears to have been suggested first in 1867 by Borlinetto,[65] who proposed a mixture of picric acid 35 per cent, sodium nitrate 35 per cent, and potassium chromate 30 per cent for use in mining. Sprengel in 1873 reported that picric acid in conjunction with suitable oxidizing agents is a powerful explosive. In 1885 Turpin[66] patented its use, both compressed and cast, in blasting cartridges and in shells, and shortly thereafter the French government adopted it under the name of *mélinite*. In 1888 Great Britain commenced to use it under the name of *lyddite*. Cast charges require a booster, for which purpose compressed picric acid or tetryl is generally used. The loading of picric acid into shells by pouring is open to two objections, which, however, are not insuperable, namely, the rather high temperature of the melt and the fact that large crystals are formed which may perhaps cause trouble on setback. Both difficulties are met by adding to the picric acid another explosive substance which lowers its melting point. Mixtures are preferred which melt between 70° and 100°, above 70° in order that exudation may be less likely and below 100° in order that the explosive may be melted by hot water. The mixtures are not necessarily eutectics. Two of the favorite French explosives have been DD 60/40, which consists of 60 parts picric acid and 40 parts dinitrophenol; and *crésylite* 60/40, 60 parts trinitro-*m*-cresol and 40 parts picric acid. Others are MDPC, picric acid 55 parts, dinitrophenol 35, and trinitro-*m-cresol* 10; and MTTC, which has the same composition as MDPC except that TNT is used instead of dinitrophenol. All these mixtures melt between

[65] Giua, *op. cit.*, pp. 287, 296.
[66] Fr. Pat. 167,512 (1885).

80° and 90° and are prepared by putting the materials together under water in wooden tanks and blowing in live steam. The water is sometimes acidulated with sulfuric acid to insure the removal of all metallic picrates. An explosive made by mixing 88 parts of picric acid with 12 parts of melted paraffin or stearic acid, and then rolling and graining, gives a compact charge when loaded by compression. It is nearly as powerful and brisant as picric acid, and responds satisfactorily to the impulse of the detonator, but is distinctly less sensitive to mechanical shock.

### Ammonium Picrate

Ammonium picrate is less sensitive to shock than picric acid. It is not easily detonated by fulminate, but is commonly used with a

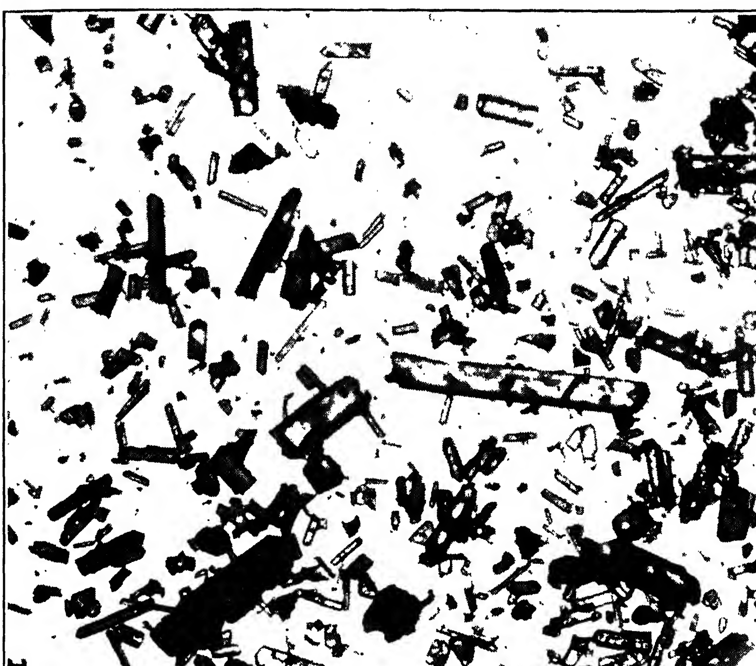


FIGURE 49. Commercial Sample of Ammonium Picrate (25×).

booster of powdered and compressed picric acid or tetryl. The pure substance occurs in two forms, a stable form which is of a

bright lemon yellow color and a meta-stable form which is a brilliant red. These differ slightly in their crystal angles but show no detectable difference in their explosive properties. Thallium picrate similarly exists in two forms.

Ammonium picrate is prepared by suspending picric acid in a convenient quantity of hot water, adding strong ammonia water until everything goes into solution and a large excess of ammonia is present, and allowing to cool. The crystals which separate are the red form. A dry sample of this material in a stoppered bottle will remain without apparent change for many years. In contact with its saturated aqueous solution it changes to the yellow form during several months. The yellow form of ammonium picrate is best procured by recrystallizing the red form several times from water.

Pure ammonium picrate melts with decomposition at 265-271°. It is more soluble in warm alcohol than guanidine picrate is, and more soluble in acetone than in alcohol, but it goes into solution very slowly in alcohol and crystallizes out again very slowly when the liquid is allowed to stand.

Solubility of Ammonium Picrate

(Grams per 100 cc. of solution)

| Temperature, °C. | Ethyl Acetate | Ethyl Alcohol |
|---|---|---|
| 0 | 0.290 | 0.515 |
| 10 | 0.300 | 0.690 |
| 20 | 0.338 | 0.850 |
| 30 | 0.380 | 1.050 |
| 40 | 0.420 | 1.320 |
| 50 | 0.450 | 1.890 |
| 60 | 0.500 | 2.165 |
| 70 | 0.540 | 2.760 |
| 80 | 0.560 | 3.620 |

## Guanidine Picrate

Guanidine picrate is procured as a yellow, finely crystalline precipitate by mixing warm solutions of guanidine nitrate and ammonium picrate. It is even less sensitive to blow and to shock than ammonium picrate; it is not detonated by fulminate and is used with a picric acid booster. The pure material, recrystallized from alcohol or from water, in both of which solvents it is sparingly soluble, melts with decomposition at 318.5-319.5°.

SOLUBILITY OF GUANIDINE PICRATE

(Grams per 100 cc. of solution)

| Temperature, °C. | Water | Ethyl Alcohol | Acetone |
|---|---|---|---|
| 0 | 0.005 | 0.077 | 0.455 |
| 10 | 0.038 | 0.093 | 0.525 |
| 20 | 0.070 | 0.122 | 0.605 |
| 30 | 0.100 | 0.153 | 0.695 |
| 40 | 0.150 | 0.200 | 0.798 |
| 50 | 0.230 | 0.255 | 0.920 |
| 60 | 0.350 | 0.321 | 1.075 |
| 70 | 0.480 | 0.413 | ... |
| 80 | 0.700 | 0.548 | ... |
| 90 | 1.010 | ... | ... |
| 100 | 1.380 | ... | ... |

### Trinitrocresol (cresylite)

This explosive is prepared from *m*-cresol by a process entirely similar to that by which picric acid is prepared from phenol. The pure material is readily soluble in alcohol, ether, and acetone, soluble in 449 parts of water at 20° and in 123 parts at 100°, yellow needles from water, m.p. 107°. The ammonium salt, which is sparingly soluble in water, has been used in the composition of certain ammonium nitrate explosives, and it was adopted by the Austrian monarchy under the name of *ecrasite* as an explosive for shells of large caliber.

### Trinitroresorcinol (styphnic acid)

Resorcinol nitrates readily to the trinitro compound, yellow prisms from water or alcohol, m.p. 175.5°. Styphnic acid is more expensive and less powerful than picric acid. Liouville[67] found that styphnic acid exploded in a manometric bomb, at a density of loading of 0.2, gave a pressure of 2260 kilos per sq. cm., whereas picric acid under the same conditions gave a pressure of 2350 kilos per sq. cm. It did not agglomerate to satisfactory pellets under a pressure of 3600 kilos per sq. cm. It is a fairly strong dibasic acid, and its salts are notably more violent explosives than the picrates. Lead styphnate has been used to facilitate the ignition of lead azide in detonators.

### Trinitroanisol and Trinitrophenetol

2,4,6-Trinitroanisol (2,4,6-trinitrophenyl methyl ether, methyl picrate) has explosive properties comparable with those of picric

[67] *Mém. poudres,* 9, 139 (1897-1898).

acid and trinitrocresol, but it contains no hydroxyl group and does not attack metals readily with the formation of dangerously explosive salts. In actual use, however, it reacts slowly with moisture and yields some picric acid. It has been colloided with nitrocellulose in the form of a strip powder, flashless and of low hygroscopicity, but the powder in the course of time developed enough picric acid to stain the fingers and to give a yellow solution with water. Its relatively low melting point, 67-68°, gives it an advantage over picric acid for certain purposes. Methyl alcohol is needed for its synthesis, and the present availability of this substance cheaply from high-pressure synthesis further commends it. While anisol is an expensive raw material, and has the further disadvantage that its direct nitration is dangerous, trinitroanisol may be prepared, without it, economically and easily from benzene through the use of dinitrochlorobenzene.

Trinitroanisol was prepared by Cahours[68] in 1849 by the direct nitration of anisol, and the same process has been studied more recently by Broadbent and Sparre.[69] The strongly *ortho-para* orienting methoxy group promotes substitution greatly, the first products of the nitration are explosive, and the temperature of the reaction mixture during the first stages ought never to be allowed to rise above 0°. A small drop of anisol, or of phenetol or other aromatic-aliphatic ether, added to 10 cc. of nitric acid (*d.* 1.42) in a test tube and shaken, causes a remarkable series of color changes; the liquid turns yellow, then green, then blue, and finally reddish purple. A batch of anisol which was being nitrated at ordinary temperature in the author's laboratory detonated without warning and without provocation while showing a bluish-purple color. Small pieces of the 2-liter flask which had contained the mixture were propelled so violently that they punctured the plate-glass windows of the laboratory without, however, breaking or cracking them.

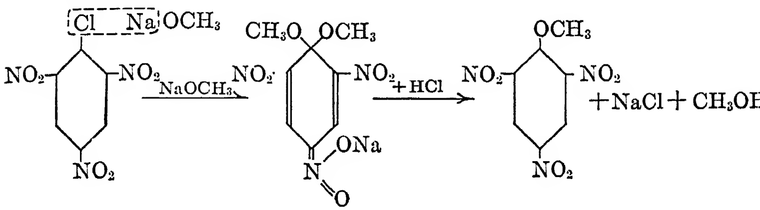
Trinitroanisol may also be prepared by the interaction of methyl iodide and silver picrate, and by the nitration of anisic acid, during which the carboxyl group is lost, but the most convenient method appears to be that of Jackson[70] and his collaborators by which a methoxy group is substituted for chlorine in a nucleus already nitrated. A methyl alcohol solution of picryl

[68] *Ann.*, 69, 236 (1849).

[69] *Eighth Intern. Congr. Appl. Chem.*, 4, 15 (1912).

[70] *Am. Chem. J.*, 20, 448 (1898); 23, 294 (1901).

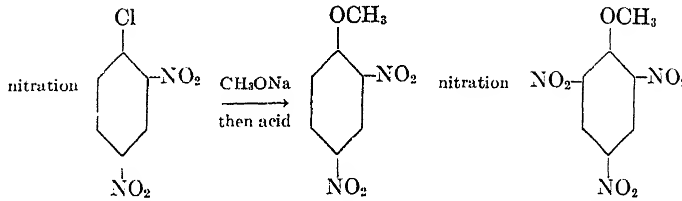
chloride, treated with an excess of sodium methylate or of strong caustic soda solution, turns dark red and deposits handsome brilliant red crystals of the empirical composition, trinitroanisol·$NaOCH_3$. The probable constitution of these crystals is indicated below. On treatment with acid the substance yields trinitroanisol.



The red material is sparingly soluble in alcohol and in water, and is easily decomposed by aqueous acids. It is a primary explosive, stable to moderate heating but decomposing at 165° and exploding violently when introduced into a flame. It is not altered by dry air, but water decomposes it slowly to form first trinitroanisol and later picric acid. On boiling with ethyl alcohol, it yields the sodium ethylate addition product of trinitrophenetol—an interesting reaction analogous to the *ester interchange* in the aliphatic series.

*Preparation of Trinitroanisol.* Thirty-five grams of picryl chloride is dissolved in 400 cc. of methyl alcohol with warming under reflux, and the solution is allowed to cool to 30-35°. A solution of 23 grams of sodium hydroxide in 35 cc. of water is added slowly through the condenser, while the liquid is cooled, if need be, to prevent it from boiling. The mixture is allowed to stand for an hour or two. The red precipitate is filtered off, washed with alcohol, and stirred up with water while strong hydrochloric acid is added until all red color has disappeared. The slightly yellowish, almost white, precipitate, washed with water for the removal of sodium chloride, dried, and recrystallized from methyl alcohol, yields pale yellow leaflets of trinitroanisol, m.p. 67-68°. From anhydrous solvents the substance separates in crystals which are practically white.

Since the methoxy group exercises a greater effect in promoting substitution than the chlorine atom does, it is to be expected that dinitroanisol would take on a third nitro group more easily than dinitrochlorobenzene (to form picryl chloride), and with less expense for acid and for heat. The reactions indicated below are probably the best for the large-scale commercial production of trinitroanisol.



During the first World War the Germans used a mixture of trinitroanisol and hexanitrodiphenyl sulfide in bombs.[71]

Trinitrophenetol or ethyl picrate, m.p. 78°, is prepared by the same methods as trinitroanisol. The explosive properties of the two substances have been studied by Desparmets and Calinaud, and by Desvergnes,[72] who has reported the results of the earlier workers together with data of his own and discussions of methods of manufacture and of the explosive properties of mixtures with picric acid, ammonium nitrate, etc. Drop test with a 5-kilogram weight were as follows:

| | Height of Drop, Centimeters | Per Cent Explosion |
|---|---|---|
| Picric acid......... | 30 | 50 |
| Trinitroanisol...... | 100 | 20 |
| Trinitroanisol...... | 110 | 30 |
| Trinitrophenetol.... | 100 | 10 |
| Trinitrophenetol.... | 110 | 10 |

Velocities of detonation (densities not reported) were trinitroanisol 7640 meters per second, trinitrophenetol 6880, and, for comparison, TNT 6880 meters per second. Pellets of the compressed explosives fired in the manometric bomb gave the results tabulated below.

| | Density of Loading | Pressure: Kilos Per Square Centimeter |
|---|---|---|
| Picric acid........... | 0.20 | 2310 |
| Picric acid........... | 0.20 | 2350 |
| Picric acid........... | 0.20 | 2210 |
| Trinitroanisol........ | 0.20 | 2222 |
| Trinitroanisol........ | 0.20 | 2250 |
| Trinitroanisol........ | 0.20 | 2145 |
| Trinitrophenetol...... | 0.20 | 1774 |
| Picric acid........... | 0.25 | 3230 |
| Trinitroanisol........ | 0.25 | 2850 |
| Trinitrophenetol...... | 0.25 | 2490 |
| Trinitrophenetol...... | 0.30 | 3318 |

[71] Desvergnes, *Mém. poudres*, 19, 283 (1922).
[72] *Ibid.*

Both trinitroanisol and trinitrophenetol were found to be as satisfactory as compressed TNT for use as a booster charge in 75-mm. shells loaded with *schneiderite*.

### Trinitroaniline (picramide)

2,4,6-Trinitroaniline, orange-red crystals from alcohol, m.p. 186°, has but little interest as an explosive for the reason that other more powerful and more valuable explosives may be prepared from the same raw materials. It may be prepared by nitrating aniline in glacial acetic acid solution or by the use of mixed nitric-sulfuric acid in which no large excess of sulfuric acid is present. The presence of nitrous acid must be avoided, as this attacks the amino group, replaces it by hydroxyl, and results in the formation of picric acid. The nitration of aniline in the presence of a large amount of concentrated sulfuric acid yields *m*-nitroaniline[73] and later the nitro compounds which are derived from it.

### Tetranitroaniline (TNA)

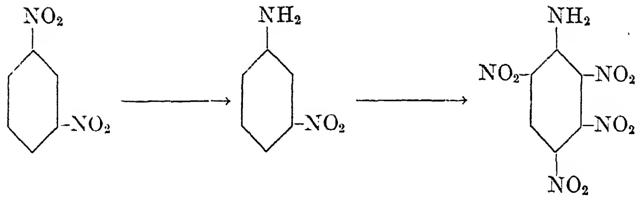
2,3,4,6-Tetranitroaniline, discovered by Flurscheim,[74] has interesting explosive properties but is such a reactive chemical substance that, when all things are considered, it is unsuitable for use. It was used to some extent during the first World War and was studied very thoroughly at that time.

Flurscheim prepared TNA by a one-stage nitration[75] of *m*-nitroaniline sulfate, that substance being procured by the reduction of *m*-dinitrobenzene with sodium polysulfide. The nitration proceeds smoothly, and the entering groups take the positions indicated by the strongly ortho-para orienting amino group. The yield is about 120 per cent of the weight of the *m*-nitroaniline.

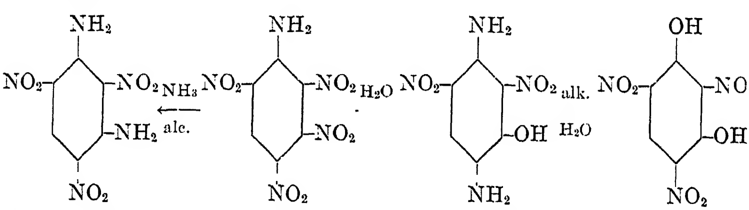
[73] van Duin, *Rec. trav. chim.*, 37, 111 (1917).

[74] *Chem. News*, 1910, 218; Brit. Pats. 3224, 3907 (1910); Ger. Pats. 241,697, 243,079 (1912); U. S. Pat. 1,045,012 (1912); *Z. ges. Schiess- u. Sprengstoffw.*, 1913, 185; *Mon. Sci.*, 1914, 490.

[75] Other studies on the nitration: Stettbacher, *Z. ges. Schiess- u. Sprengstoffw.*, 11, 114 (1916); van Duin, *loc. cit.* A laboratory method for the preparation of TNA direct from aniline is described in Stettbacher's book, *op. cit.*, p. 201.



Pure TNA, yellowish-brown or greenish-brown crystals from acetone, melts with decomposition at about 210° and deflagrates at about 226°. It is soluble in glacial acetic acid (1 part in 24 at boiling temperature), readily in acetone (1 in 6 at boiling temperature), and sparingly in benzene, ligroin, and chloroform. If a small amount of water is added to an acetone solution of TNA and the liquid is refluxed, the nitro group in the 3-position, having other nitro groups *ortho* and *para* to it, is replaced rapidly by hydroxyl. The resulting trinitroaminophenol, m.p. 176°, is capable of attacking metals to form dangerous explosive salts which are similar to the picrates. If TNA is boiled with aqueous sodium carbonate or bicarbonate both the amino group and the nitro group in the 3-position are hydrolyzed, and trinitroresorcinol is formed.



With alcoholic ammonia TNA yields trinitro-*m*-phenylenediamine, m.p. 288°. Its nitro group in the 3-position reacts with primary and secondary amines, with sodium acid sulfite, etc., in the same way that the *meta* nitro groups of $\beta$- and $\gamma$-trinitrotoluene do. Marqueyrol found that TNA is attacked rapidly by boiling water, about half of it being converted into trinitroaminophenol, the other half being destroyed with the evolution of gases, largely carbon dioxide and nitrogen along with smaller quantities of carbon monoxide, hydrocyanic acid, and nitric oxide. At 75° the reaction between water and TNA is complete after 4 days; at 60° it is about half complete after 7 days; at 40° it is appreciable after 10 days. Any decomposition of this sort, of course, is too much for an explosive intended for military use.

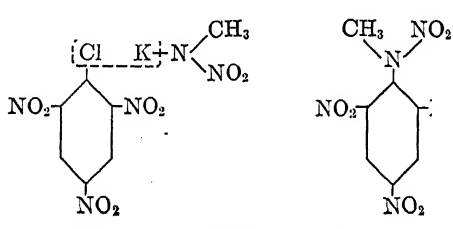
TNA shows about the same sensitivity as tetryl in the drop test. Lead block experiments have been reported which showed that 10 grams of TNA produced a net expansion of 430 cc., TNT 254 cc., picric acid 297 cc., tetryl 375 cc., guncotton 290 cc., and 75 per cent dynamite 300 cc.[76] Experiments with the manometric bomb gave the results indicated below.

| | Density of Loading | Pressure: Kilos per Square Centimeter |
|---|---|---|
| TNA........... | 0.20 | 2356 |
| TNA........... | 0.25 | 3110 |
| Tetryl.......... | 0.20 | 2423 |
| Tetryl.......... | 0.25 | 3243 |

Since these data show that tetryl is slightly more powerful than TNA, the superiority of TNA in the lead block test must be interpreted as indicating that TNA has the higher velocity of detonation.

**Tetryl** (tetralite, pyronite)

Tetryl or 2,4,6-trinitrophenylmethylnitramine was first described by Michler and Meyer[77] in 1879, and was studied soon thereafter by van Romburgh[78] and by Mertens.[79] Van Romburgh proved its structure by synthesizing it from picryl chloride and potassium methylnitramine.



In the early literature of the subject, and to some extent at present, the substance is wrongly designated as tetranitromethylaniline. It results from the nitration of monomethyl- and of

[76] From the pamphlet "Tetra-Nitro-Aniline 'Flurscheim,'" Verona Chemical Company, sole licensed manufacturers for the United States, North Newark, New Jersey, 1917(?), p. 4. Giua, *op. cit.*, p. 317, states that the force of TNA measured in the lead block is 420 compared with picric acid 297.

[77] *Ber.*, **12**, 1792 (1879).

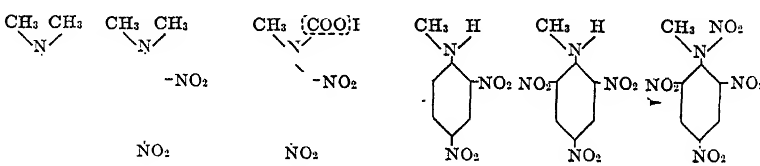
[78] *Rec. trav. chim.*, **2**, 108 (1883); **6**, 215 (1887).

[79] *Ber.*, **19**, 2126 (1886).

dimethylaniline, and is prepared industrially by the nitration of the latter. The course of the reactions is first the introduction of two nitro groups in the nucleus, then the removal of one of the

FIGURE 50. Commercial Sample of Tetryl (20×). Material crystallized in this form pours easily and may be made into pellets by machinery.

methyl groups by oxidation, then the introduction of a third nitro group in the nucleus, and finally the replacement of the amino hydrogen by a nitro group.



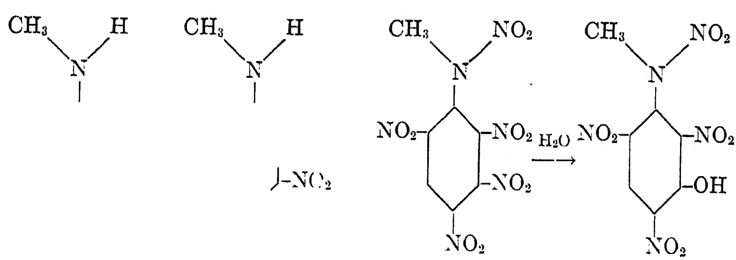
All the above-indicated intermediates have been isolated from the reaction. The last step is interesting because it is a reversible nitration. If tetryl is dissolved in concentrated (95 per cent) sulfuric acid and allowed to stand, the nitro group on the nitrogen is replaced by hydrogen, and nitric acid and trinitromethylaniline (methylpicramide), m.p. 111.8-112.4°, are formed.[80] Tetryl accordingly gives up this nitro group, and only this one, in the nitrometer. In the industrial preparation of tetryl, the usual method is to dissolve the dimethylaniline in concentrated sulfuric acid and then to carry out all the reactions in one stage. The process has been the subject of many careful studies, among which those of Langenscheidt,[81] van Duin,[82] Knowles,[83] Wride,[84] Desvergnes,[85] and Bain[86] are especially to be noted. The crude tetryl contains impurities which must be removed by boiling the finely comminuted substance in water, and by dissolving the crude material in benzene and filtering for the removal of insoluble materials. For the industrial crystallization of tetryl, either acetone or benzene is commonly used.

*Preparation of Tetryl.* Twenty grams of dimethylaniline is dissolved in 240 grams of concentrated sulfuric acid (*d.* 1.84), the temperature being kept below 25°, and the solution is allowed to run from a separatory funnel drop by drop into 160 grams of 80 per cent nitric acid (*d.* 1.46), previously warmed to 55° or 60°, while this is stirred continuously and kept at a temperature between 65° and 70°. The addition requires about an hour. After all has been added, the stirring is continued while the temperature of the mixture is maintained at 65° to 70°. The material is allowed to cool; the solid matter is collected on an asbestos filter, washed with water, and boiled for an hour with 240 cc. of water while further water is added from time to time to replace that which boils away. The crude tetryl is filtered off, ground under water to pass a 150-mesh sieve, and boiled twice for 4 hours each time with 12 times its weight of water. The solid is dried and treated with benzene sufficient to dissolve all readily soluble material. The solution is filtered and allowed to evaporate spontaneously, and the residue is recrystal-

[80] Davis and Allen, *J. Am. Chem. Soc.*, **46**, 1063 (1924).
[81] *Z. ges. Schiess- u. Sprengstoffw.*, **7**, 445 (1912).
[82] *Rec. trav. chim.*, **37**, 111 (1917).
[83] *J. Ind. Eng. Chem.*, **12**, 247 (1920).
[84] *Arms and Explosives*, 1920, 6.
[85] *Mém. poudres*, **19**, 217 (1922).
[86] *Army Ordnance*, **6**, 435 (1926).

lized from alcohol. Pure tetryl melts at about 129.4°; a good commercial sample, at about 128.5°.

The nitration of aniline in the presence of a large amount of strong sulfuric acid results wholly in the formation of *m*-nitroaniline, but the similar nitration of dimethylaniline gives principally a mixture of the *ortho-* and *para*-derivatives. Monomethylaniline stands between aniline and dimethylaniline in respect to the orienting effect of its amino group; it yields a considerable amount of the *m*-nitro- compound—and dimethylaniline is preferred for the preparation of tetryl. Commercial dimethylaniline contains a certain amount of monomethylaniline, from which it is extremely difficult to free it, and this in the manufacture of tetryl is converted in part into 2,3,4,6-tetranitrophenylmethylnitramine, or *m*-nitrotetryl, pale yellow, almost white, crystals from benzene, m.p. 146-147.°[87]

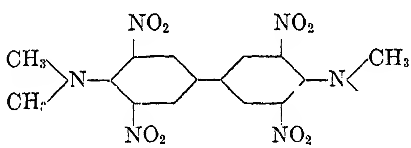


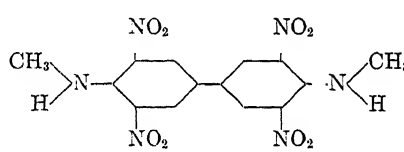
No *m*-nitrotetryl is produced if pure dimethylaniline is used in the usual process for the manufacture of tetryl. The amount of this impurity in the usual process depends upon the amount of monomethylaniline which may be present. A large excess of sulfuric acid tends toward the production of *m*-nitro compounds, but a reduction in the amount of sulfuric acid is not feasible for this increases the amount of benzene-insoluble material. *m*-Nitrotetryl reacts with water, as TNA does; the nitro group in the 3-position is replaced by hydroxyl, and *m*-hydroxytetryl or 2,4,6-trinitro-3-methylnitraminophenol, yellow crystals from water, m.p. 183°, is formed. This substance resembles picric acid and forms explosive salts. It is readily soluble in water, and

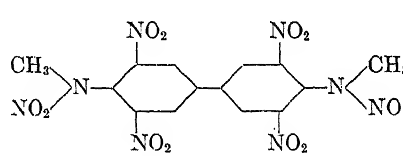
[87] Van Romburgh, *Rec. trav. chim.*, 8, 274 (1889). Van Romburgh and Schepers, *Versl. Kon. Akad. Wetenschapen*, 22, 293 (1913), also prepared this substance by the nitration of dimethylaniline (in 20 times its weight of concentrated sulfuric acid).

*m*-nitrotetryl is effectively removed from crude tetryl by boiling the finely powdered solid with water.

Crude tetryl commonly contains a small quantity of amorphous-appearing, buff-colored material of high melting point which is insoluble in benzene. The amount of this material is increased by the presence of larger amounts of water in the nitrating acid. Michler and Pattinson[88] found that tetramethylbenzidine is produced when dimethylaniline is heated with concentrated sulfuric acid. The same material is evidently formed during the preparation of tetryl and gives rise to the three substances indicated below, which constitute the benzene-insoluble impurity.







III

These substances were prepared by Mertens[89] in 1886 by the action of nitric acid on dimethylaniline (I, II, and III) and on monomethylaniline (II and III). Van Romburgh[90] in the same year proved them to be derivatives of benzidine, and at a much later time[91] summarized the work which had been done upon them and synthesized the substances in such manner as to prove the position of the nitro groups.

[88] *Ber.*, 14, 2161 (1881).
[89] *Loc. cit.*
[90] *Rec. trav. chim.*, 5, 240 (1886).
[91] *Ibid.*, 41, 38 (1922).

If the benzene-insoluble material from crude tetryl is dissolved in hot fuming nitric acid and allowed to cool, glistening yellow crystals are procured. These, recrystallized from nitric acid and then from acetone with the addition of two volumes of ligroin, yield cream-colored small crystals of the third of the above-indicated substances, 3,3′,5,5′-tetranitro-4,4′-di-(methylnitramino)-biphenyl, or 3,3′,5,5′-tetranitrodimethylbenzidinedinitramine. The material decomposes with foaming at 229-230° if its temperature is raised at the rate of 6° per minute. If it is heated more slowly, at 2° per minute, it melts partially and decomposes at 222° with preliminary softening and darkening. Like tetryl and other nitroamines, it gives a blue color with the diphenylamine reagent. Although Willstätter and Kalk[92] have found that monomethylaniline is not convertible into a benzidine derivative by Michler's method, it is nevertheless true that the benzene-insoluble by-products are produced during the preparation of tetryl from monomethylaniline, as indeed Mertens first procured them by the action of nitric acid on that substance.

The usual process for the preparation of tetryl from dimethylaniline has the disadvantage that the by-products, namely, the *m*-nitrotetryl and the benzene-insoluble material, necessitate a rather elaborate purification, and it has the further disadvantage that one of the methyl groups of the dimethylaniline is destroyed by oxidation (expense) with the production of red fumes (nuisance) and the consequent loss of valuable combined nitrogen. All these disadvantages find their origin at points in the reaction earlier than the formation of dinitromonomethylaniline. 2,4-Dinitromonomethylaniline, orange-yellow crystals, m.p. 174°, nitrates smoothly to form tetryl without the production of by-products or red fumes. Synthetic methyl alcohol is now available cheaply and in a quantity which is limited only by the will of the manufacturers to produce it. It reacts with ammonia (from the fixation of nitrogen) at elevated temperatures in the presence of a thorium oxide catalyst to form methylamine,[93] and methylamine reacts with dinitrochlorobenzene to form dinitromonomethylaniline. There seems every reason to believe that tetryl in the future will be manufactured chiefly, or wholly, from dinitrochlorobenzene.

[92] *Ber.*, 37, 3771 (1904).

[93] Davis and Elderfield, *J. Am. Chem. Soc.*, 50, 1786 (1928).

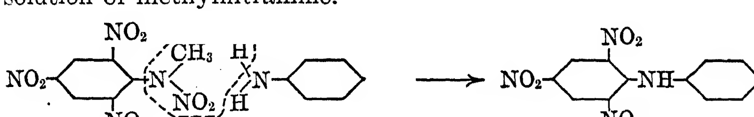
The solubility of tetryl in various solvents is tabulated below.

SOLUBILITY[94] OF TETRYL

(Grams per 100 grams of solvent)

| Temperature, °C. | Water | 95% Alcohol | Carbon Tetrachloride | Chloroform | Carbon Disulfide | Ether |
|---|---|---|---|---|---|---|
| 0 | 0.0050 | 0.320 | 0.007 | 0.28 | 0.0090 | 0.188 |
| 5 | 0.0058 | 0.366 | 0.011 | 0.33 | 0.0120 | 0.273 |
| 10 | 0.0065 | 0.425 | 0.015 | 0.39 | 0.0146 | 0.330 |
| 15 | 0.0072 | 0.496 | 0.020 | 0.47 | 0.0177 | 0.377 |
| 20 | 0.0075 | 0.563 | 0.025 | 0.57 | 0.0208 | 0.418 |
| 25 | 0.0080 | 0.65 | 0.031 | 0.68 | 0.0244 | 0.457 |
| 30 | 0.0085 | 0.76 | 0.039 | 0.79 | 0.0296 | 0.493 |
| 35 | 0.0094 | 0.91 | 0.048 | 0.97 | 0.0392 | ... |
| 40 | 0.0110 | 1.12 | 0.058 | 1.20 | 0.0557 | ... |
| 45 | 0.0140 | 1.38 | 0.073 | 1.47 | 0.0940 | ... |
| 50 | 0.0195 | 1.72 | 0.095 | 1.78 | ... | ... |
| 55 | 0.0270 | 2.13 | 0.124 | 2.23 | ... | ... |
| 60 | 0.0350 | 2.64 | 0.154 | 2.65 | ... | ... |
| 65 | 0.0440 | 3.33 | 0.193 | ... | ... | ... |
| 70 | 0.0535 | 4.23 | 0.241 | ... | ... | ... |
| 75 | 0.0663 | 5.33 | 0.297 | ... | ... | ... |
| 80 | 0.0810 | ... | ... | ... | ... | ... |
| 85 | 0.0980 | ... | ... | ... | ... | ... |
| 90 | 0.1220 | ... | ... | ... | ... | ... |
| 95 | 0.1518 | ... | ... | ... | ... | ... |
| 100 | 0.1842 | ... | ... | ... | ... | ... |

Tetryl is hydrolyzed rapidly by boiling aqueous sodium carbonate to form sodium picrate, sodium nitrite, and methylamine which escapes. It is not affected by prolonged boiling with dilute sulfuric acid. It reacts with aniline in benzene solution at ordinary temperature; red crystals of 2,4,6-trinitrodiphenylamine, m.p. 179.5-180°, separate after the liquid has stood for a few hours, and extraction of the liquid with water yields an aqueous solution of methylnitramine.



By heating tetryl alone, Farmer[95] and Desvergnes[96] obtained picric acid, and by heating tetryl in high-boiling solvents Mer-

[94] Taylor and Rinkenbach, *J. Am. Chem. Soc.*, **45**, 104 (1923).
[95] *J. Chem. Soc.*, **117**, 1603 (1920).
[96] *Loc. cit.*

tens,[96] van Romburgh,[96] and Davis and Allen[96] obtained methylpicramide. When refluxed in xylene solution, tetryl gives off nitrous fumes and is converted into a tarlike mass from which picric acid and methylpicramide may be isolated, along with a third, unidentified, buff-colored finely crystalline substance which melts at 240.5°. If pure tetryl is kept at 100°, it gives off nitrous fumes and a small quantity of formaldehyde, and yields after 40 days a mass which remains semi-liquid at ordinary temperature. By heating at 125° it is converted into a viscous liquid after about the same number of hours.

At ordinary temperatures tetryl appears to be perfectly stable. Current methods of purification insure the absence of occluded acid. It is more powerful and more brisant than TNT and picric acid, though distinctly more sensitive to shock, and is probably the best of all the common explosives for use in boosters and reinforced detonators. Koehler[97] reports pressures in the manometric bomb (density of loading = 0.3) and temperatures produced by the explosions, as follows:

| | Pressure: Kilos per Square Centimeter | Temperature, °C. |
|---|---|---|
| Tetryl......... | 4684 | 2911 |
| Picric acid...... | 3638 | 2419 |
| TNT.......... | 3749 | 2060 |
| TNB.......... | 3925 | 2356 |

Aranaz[98] reports that the explosion of tetryl produces a temperature of 3339°. Tetryl is slightly more sensitive than picric acid, and considerably more sensitive than TNT, in the drop test. Experimenting with a 5-kilogram weight, Koehler found that a drop of 150 cm. caused the detonation of tetryl 10 times out of 10 trials, a drop of 100 cm. 9 times out of 10, of 50 cm. 5 times out of 10, and of 40 cm. 3 times out of 10. Martin[99] has determined the minimum charges of various primary explosives necessary for the detonation of TNT and tetryl. The explosives were loaded into detonator capsules, and the initiators were compressed upon them at a pressure of 1100 kilos per square centimeter.

[97] Cited by Desvergnes, *loc. cit.*

[98] Aranaz, "Les nuevos explosivos," Madrid, 1911, cited by Desvergnes.

[99] Martin, "Ueber Azide und Fulminate," Darmstadt, 1913, cited by Giua, *op. cit.*, p. 320.

| | Minimum Charge for Detonation of TNT | Tetryl |
|---|---|---|
| Mercuric fulminate........ | 0.36 | 0.29 |
| Silver fulminate........... | 0.095 | 0.02 |
| Cadmium fulminate....... | 0.11 | 0.008 |
| Mercurous azide........... | 0.145 | 0.045 |
| Silver azide............... | 0.07 | 0.02 |
| Lead azide................ | 0.09 | 0.025 |
| Cadmium azide........... | 0.04 | 0.01 |

With each of the initiators which was tried, tetryl was more easily detonated than TNT. Taylor and Cope[100] have determined the minimum charges of fulminate-chlorate (90:10) necessary to cause the complete detonation of various mixtures of TNT and tetryl, as follows:

| Mixture of TNT-Tetryl | | Weight of Initiator, Grams |
|---|---|---|
| 100 | 0 | 0.25 |
| 90 | 10 | 0.22 |
| 80 | 20 | 0.21 |
| 50 | 50 | 0.20 |
| 0 | 100 | 0.19 |

**"Ethyl Tetryl."** 2,4,6-Trinitrophenylethylnitramine

The ethyl analogue of tetryl was first prepared by van Romburgh,[101] who procured it both by nitrating monoethylaniline and by nitrating diethylaniline, and reported that it melts at 96°. The present writer has found that the pure material, recrystallized twice from nitric acid (*d.* 1.42) and once from alcohol, melts at 94°. It is comparable to tetryl in its chemical reactions and in its explosive properties.

**"Butyl Tetryl."** 2,4,6-Trinitrophenyl-*n*-butylnitramine

The *n*-butyl analogue of tetryl[102] has been prepared by two methods: (*a*) by condensing 2,4-dinitrochlorobenzene with *n*-butylamine to form 2,4-dinitro-*n*-butylaniline,[103] and by the nitration of this product; and (*b*) by the nitration in one step of *n*-butylaniline. The pure substance crystallizes from alcohol in

[100] *U. S. Bureau of Mines Technical Paper 145,* Washington, 1916.
[101] *Rec. trav. chim.,* 2, 111 (1883).
[102] Davis, U. S. Pat. 1,607,059 (1926).
[103] Pure 2,4-dinitro-*n*-butylaniline crystallizes from alcohol in deep yellow or orange needles, m.p. 92.5-93.0°.

lemon-yellow plates which melt at 97.5-98.0°. It is readily soluble in benzene, ethyl acetate, alcohol and acetone, and is insoluble in petroleum ether. It yields sodium picrate when boiled with sodium carbonate solution.

Butyl tetryl is suitable for use in boosters, reinforced detonators, detonating fuse, primer caps, etc. For the detonation of 0.4 gram, it requires 0.19 gram of mercury fulminate. It has a slightly greater shattering effect than TNT in the sand test and shows about the same sensitivity as tetryl in the drop test. It explodes spontaneously at 210°.

### Hexanitrodiphenylamine

2,2′,4,4′,6,6′-Hexanitrodiphenylamine (hexil, hexite, hexamin, etc.) is another explosive which can be prepared most conveniently from dinitrochlorobenzene. Its ammonium salt has been used under the name of *aurantia* as a yellow dye for silk and wool. It has valuable explosive properties but is more poisonous than nitroglycerin and attacks the skin, causing severe blisters which resemble burns. Its dust is injurious to the mucous membranes of the mouth, nose, and lungs. Mertens[104] in 1878 prepared hexanitrodiphenylamine by the nitration of diphenylamine with fuming nitric acid in concentrated sulfuric acid solution. Its behavior as a pseudo-acid has been studied by Alexandrov[105] and by Hantzsch and Opolski.[106] Hausermann[107] in 1891 reported upon its explosive power as compared with trinitrotoluene, and a patent granted in 1909 to Otto Freiherr von Schroetter[108] described an explosive consisting of 80 parts of hexanitrodiphenylamine and 20 parts of trinitrotoluene. The large-scale preparation by the direct nitration of diphenylamine was reported in 1910,[109] and the process from dinitrochlorobenzene, originally described in a patent to the Griesheim Chem. Fabrik,[110] was reported by

[104] *Ber.*, **11**, 843 (1878). Austen, *ibid.*, **7**, 1249 (1874), reported the formation of the substance by the nitration of picryl-*p*-nitroaniline, and Gnehm, *ibid.*, **7**, 1399 (1874), by the nitration of methyldiphenylamine.

[105] *J. Russ. Phys. Chem. Soc.*, **39**, 1391 (1907).

[106] *Ber.*, **41**, 1745 (1908).

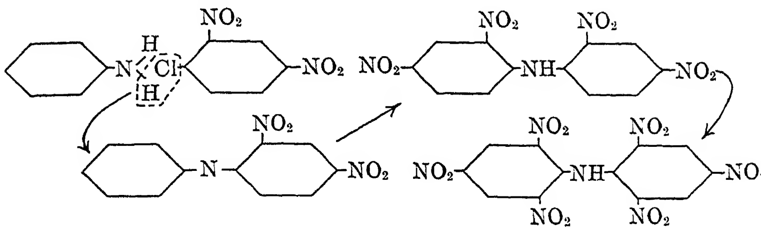
[107] *Z. angew. Chem.*, **17**, 510 (1891).

[108] U. S. Pat. 934,020 (1909).

[109] *Z. ges. Schiess- u. Sprengstoffw.*, **5**, 16 (1910).

[110] Ger. Pat. 86,295 (1895).

Carter[111] in 1913 and studied further by Hoffman and Dame[112] in 1919 and by Marshall[113] in 1920.



Dinitrochlorobenzene reacts with 2 equivalents of aniline, when the materials are warmed together in the absence of solvent or when they are stirred together vigorously with water 80-90°, to form dinitrodiphenylamine in practically quantitative yield, along with 1 equivalent of aniline hydrochloride. The use of the second molecule of aniline to combine with the hydrogen chloride involves unnecessary expense, and the same results may be accomplished by means of some mineral alkali or acid-neutralizing substance like sodium acetate or sodium or calcium carbonate. The product, which is insoluble in water, separates in bright red needles. Pure 2,4-dinitrodiphenylamine, recrystallized from alcohol or from benzene, melts at 156-157°. The crude product is nitrated in one or in two stages to the hexanitro compound.

*Preparation of Hexanitrodiphenylamine* (Two-Stage Nitration). Seventy grams of aniline and 32 grams of precipitated calcium carbonate are stirred up together with water in such manner as to form a homogeneous suspension, and the mixture is heated to about 60°. Dinitrochlorobenzene, 150 grams, previously melted, is poured in slowly in a fine stream while the stirring is continued and the mixture is heated gradually to about 90°, the rate of heating being regulated by the progress of the reaction. The product is washed with hydrochloric acid to free it from aniline and calcium carbonate, then with water until free from chlorides, and dried in the oven at 100°.

Fifty grams of finely powdered dinitrodiphenylamine is added in small portions at a time to 420 grams of nitric acid (*d.* 1.33), which is stirred vigorously while the temperature is maintained at 50-60°. The progress of the nitration is followed by observing the color change from

[111] *Z. ges. Schiess- u. Sprengstoffw.*, **8**, 205, 251 (1913).
[112] *J. Am. Chem. Soc.*, **41**, 1013 (1919).
[113] *J. Ind. Eng. Chem.*, **12**, 336 (1920).

the red of the dinitro compound to the yellow of the tetranitrodiphenylamine. After all has been added, the temperature is raised to 80-90° and kept there for 2 hours longer while the stirring is continued. After the mixture has cooled, the product is filtered off directly, washed with water until free from acid, and dried in the air or in the oven at 100°.

Fifty grams of the tetranitrodiphenylamine is added slowly, with stirring, during an hour, to a mixture of 250 grams of nitric acid (*d.* 1.50) and 250 grams of sulfuric acid (*d.* 1.83). After all has been added, the mixture is allowed to stand for 3 hours at laboratory temperature, and is then drowned in ice water. The hexanitrodiphenylamine is filtered off, washed thoroughly with water, dried in the air, and recrystallized from acetone with the addition of petroleum ether.

Pure hexanitrodiphenylamine, small yellow needles, melts with decomposition at 243.0-244.5°. It is insoluble in chloroform, sparingly soluble in ether and in cold acetic acid, fairly soluble in alcohol, and readily soluble in cold acetone and in warm acetic and nitric acids.

Marshall[114] reports minimum priming charges of fulminate-chlorate (90:10) necessary for the complete detonation of the indicated explosives to be as follows:

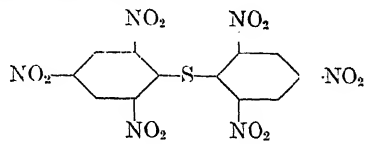
| | Grams |
|---|---|
| Hexanitrodiphenylamine | 0.18 |
| Tetryl | 0.20 |
| Tetranitroaniline | 0.20 |
| Trinitrotoluene | 0.25 |

He found hexanitrodiphenylamine to be slightly less sensitive in the drop test than tetryl and tetranitroaniline. When 1 pound of the explosive was loaded into a 3.5-inch cubical box of cardboard or tin and fired at with a U.S. Army rifle from a distance of 30 yards, hexanitrodiphenylamine gave no detonations in the cardboard boxes, and 7 detonations and 1 failure in tin; TNT gave no detonation in cardboard, fire and detonation in tin; and tetryl and tetranitroaniline gave detonations in every case with either kind of container. Marshall reported the velocity of detonation of hexanitrodiphenylamine to be 6898 meters per second at density 1.58, and 7150 meters per second at density 1.67. Pellets of the explosive, mixed with 1 per cent of stearic acid, compressed at 5000 pounds per square inch, had a density 1.43; at 10,000

[114] *Loc. cit.*

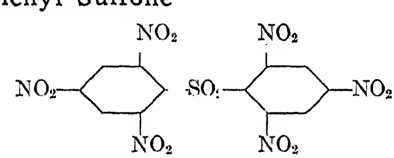
pounds per square inch, density 1.56; at 15,000 pounds per square inch, density 1.59; and at 20,000 pounds per square inch, density 1.60. The pellets which showed the best homogeneity and the least tendency to crumble were those of density 1.56.

### Hexanitrodiphenyl Sulfide




Hexanitrodiphenyl sulfide (picryl sulfide) is formed by the interaction of picryl chloride and sodium thiosulfate in alcohol solution in the presence of magnesium carbonate.[115] It is sparingly soluble in alcohol and ether, more readily in glacial acetic acid and acetone, golden-yellow leaflets from alcohol-acetone, m.p. 234°. It does not stain the fingers yellow and is said to be non-poisonous. Its explosive properties are comparable to those of hexanitrodiphenylamine. Its use in reinforced detonators has been suggested, and the fact that its explosion produces sulfur dioxide has commended it[116] for use in projectiles intended to make closed spaces, such as casemates, holds of ships, etc., untenable. During the first World War the Germans used drop bombs loaded with a mixture of equal parts of TNT and hexanitrodiphenyl sulfide.[117]

### Hexanitrodiphenyl Sulfone




The action of nitric acid on hexanitrodiphenyl sulfide yields a substance, faintly yellowish crystals, m.p. 307°, which Stettbacher believes to be the sulfone, not the peroxide as the patent[118] states, for the reason that it is stable at elevated temperatures

[115] Ger. Pat. 275,037 (1912); Brit. Pat. 18,353 (1913).

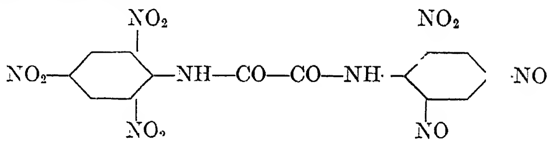
[116] Brit. Pat. 18,354 (1913).

[117] Alfred Stettbacher, "Die Schiess- und Sprengstoffe," Leipzig, 1919, p. 206.

[118] Ger. Pat. 269,826 (1913).

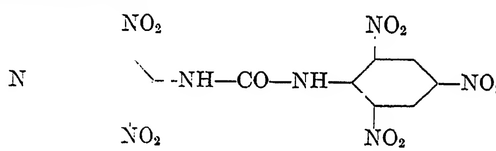
and is less sensitive to shock than the sulfide. It is a more powerful explosive than hexanitrodiphenyl sulfide.

**Hexanitro-oxanilide**



This substance, m.p. 295-300°, results from the direct nitration of oxanilide.[119] It is stable and about as powerful as TNT, and is reported to explode with the production of a temperature which is distinctly lower than that produced by many high explosives.

**Hexanitrocarbanilide**



2,2′,4,4′,6,6′-Hexanitro-N,N′-diphenylurea (hexanitrocarbanilide or *sym*-dipicrylurea)[120] may be prepared by the nitration of carbanilide (*sym*-diphenylurea) in one, in two, or in three stages. It is of interest because of its explosive properties and because it supplies one way in which benzene may be converted into an explosive which is valuable both for military and for civil uses. Carbanilide may be prepared by the interaction of aniline and phosgene but is most conveniently and economically procured by heating aniline and urea together at 160-165°.

*Preparation of Hexanitrocarbanilide* (Two Stages). Forty grams of carbanilide is dissolved in 60 cc. of concentrated sulfuric acid (*d.* 1.84), and the solution is added drop by drop during 4 hours to 96 cc. of nitric acid (*d.* 1.51) while the mixture is stirred vigorously with a mechanical stirrer and its temperature is maintained at 35° to 40°. After all has been added, the stirring is continued and the temperature is raised to 60° during half an hour and maintained at 60° for another hour. The mixture is cooled to room temperature, allowed to stand over night, then treated with cracked ice and water, and filtered. The crude tetra-

[119] Fr. Pat. 391,106.

[120] Davis, U. S. Pat. 1,568,502 (1926).

nitrocarbanilide is washed thoroughly with water and allowed to dry in the air.

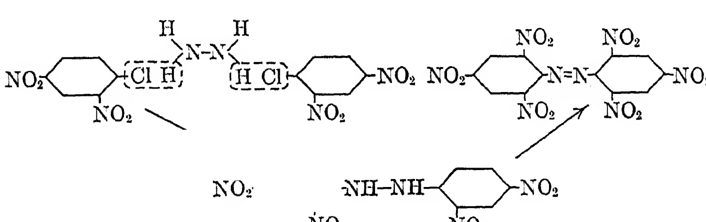
Ten grams of crude tetranitrocarbanilide is added to a mixture of 16 grams of concentrated sulfuric acid (*d.* 1.84) and 24 grams of nitric acid (*d.* 1.51), and the material is heated on the steam bath for 1 hour with constant stirring. The mixture, after cooling, is treated with cracked ice and water, and filtered. The product, washed with 500 cc. of cold water, then with 500 cc. of hot water, and dried in the air, is hexanitrocarbanilide of satisfactory quality for use as an explosive.

Pure hexanitrocarbanilide crystallizes from acetone-ligroin in pale yellow rosettes which soften and darken at 204° and melt at 208-209° with decomposition. It yields picric acid when warmed with dilute sulfuric acid, and trinitroaniline when boiled with strong ammonia water. A deep ruby-red color is developed when hexanitrocarbanilide is allowed to stand at ordinary temperatures in contact with strong ammonia water. Tetranitrocarbanilide, dinitroaniline, trinitroaniline, picric acid, and dinitrophenol do not give this color.

Hexanitrocarbanilide is a brisant high explosive suitable for use in boosters, reinforced detonators, detonating fuse, primer caps, etc. For the detonation of 0.4 gram, it requires 0.19 gram of mercury fulminate. It is slightly stronger than TNT in the sand test and of about the same sensitivity as tetryl in the drop test. It explodes spontaneously at 345°.

### Hexanitroazobenzene

Hexanitroazobenzene may be prepared from dinitrochlorobenzene and hydrazine by the reactions indicated below:



The first of these reactions takes place in hot-water suspension in the presence of sodium or calcium carbonate. The resulting tetranitrohydrazobenzene is both nitrated and oxidized by the mixed acid in the next step. Pure 2,2′,4,4′,6,6′-hexanitroazoben-

zene crystallizes from acetone in handsome orange-colored needles which melt at 215°. The explosive properties of the substance have not been reported in detail. The azo group makes it more powerful and more brisant than hexanitrodiphenylamine. The accessibility of the raw materials and the simplicity of its preparation commend it for use in boosters and compound detonators.

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